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# WATER-POLLUTION CONTROL IN THE PRIMARY NONFERROUS-METALS INDUSTRY. VOLUME I. COPPER, ZINC, AND LEAD INDUSTRIES

J. B. Hallowell, et al

Battelle Columbus Laboratories

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27 **Abstract**

The purpose ~~of the program~~ was to identify specific research needs in the area of water pollution in the primary nonferrous metals industries. This program consisted of a survey of literature and the acquisition of data from industrial operations.

The contents of the final reports (2 volumes) include: the identification of process steps using water and/or generating wastewater, the amounts of water used for various purposes, recirculation rates, amounts of wastewaters, specific or characteristic substances in wastewaters, the prevalence of wastewater treatment practice, methods, and costs; current treatment problems, and plans for future practices of recirculation or wastewater treatment.

The metals reported on included copper, lead, zinc, and associated byproducts (arsenic, cadmium, silver, gold, selenium, tellurium, sulfuric acid, salts and compounds), mercury, (primary)gold and silver, aluminum, molybdenum, and tungsten.

The information ~~presented~~ includes detailed processing descriptions and flowsheets, tabulations of quantities of water intake, quantities used by category, recirculated water, discharge water quantities and analyses, water treatment costs. Representative water flowsheets are given. ~~(Hallowell Battelle-Columbus).~~
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| | |
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# WATER-POLLUTION CONTROL IN THE PRIMARY NONFERROUS-METALS INDUSTRY

## VOLUME I. COPPER, ZINC, AND LEAD INDUSTRIES

By

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This report has been reviewed by the Environmental Protection Agency and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

## ABSTRACT

In a review of water-pollution-control practices in the primary nonferrous metallurgy industries, unpublished data were obtained on waste-water-control practices from 28 companies operating 75 separate producing plants.

Volume I of this study is concerned with the processes and water practices in the copper, lead, and zinc industries. Data supplied by 50 copper-, lead-, and zinc-producing plants showed that waste-water-control practices are influenced by climate and production processes. No waste water is discharged from many operations in the Southwestern desert area. About two-thirds of the waste waters discharged by the balance of the plants were from tailings ponds and exhibited neutral to alkaline pH. In some cases, these waste waters contained "trace" amounts of heavy metals.

The most pressing needs and problem areas identified were related to smelter-refinery-type waste waters, which were generally acid and carried metals or metalloids in the range <1 to 100 ppm. Other areas where improvements are needed include the treatment of plant sanitary wastes, accurate and economical analyses of low levels of waste-water components, expanded and improved scientific bases for setting hazard limits of heavy metals in water, and development and cost-evaluation of alternative or novel water treatment and metal and by-product production processes.

This report was submitted in fulfillment of Contract No. 14-12-870 under the sponsorship of the Office of Research and Monitoring, Environmental Protection Agency.

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## SECTION I

## CONCLUSIONS

1. Fourteen of the approximately fifty plants reviewed during the study reported zero discharge of waste water as a consequence of their location in the Southwestern desert.

2. Approximately 38 billion of the 56-1/2 billion gallons of water discharged from the balance of the 50 operations may be categorized as tailings-pond effluent ranging from neutral to alkaline and containing low levels of metals as the critical impurities.

3. The balance of discharged water is attributable to smelter-refinery operations and is highly variable in characteristics.

4. The principal area of research needs identified in this study was for treatment methods to deal with acidic waste waters containing <1 to 100 ppm of metals or metalloids, generated primarily by electrolytic refineries and by smelters. Other research needs identified included the treatment of plant sanitary wastes, accurate and economic analysis of waste water components, scientific bases for hazardous limits of heavy metals, and development of new metallurgical processes to decrease water usage or discharge.

5. The current plans of industry to improve waste water control include the approaches of total recycle, treat and discharge, and combinations of these, i.e., partial recycle with reduced discharge.

6. In only two instances were treatment plans being considered which would result in increased recovery of products.

# SECTION II

## RECOMMENDATIONS

Based on the findings of this study, it is recommended that:

1. Programs be carried out as rapidly as possible to provide cost-effectiveness evaluations of methods of treating acid, metal-bearing wastes and waste water, preferably using samples of specific operating plant wastes as exampled in this report.

2. There be developed new methods for the treatment of plant sanitary wastes, in the context of the size, surrounding resources, and water requirements of the metallurgical or industrial plant.

3. Diverse programs be undertaken to provide methods, manpower, equipment, and facilities to achieve routinely accurate, economical analyses of water down to the parts-per-billion range.

4. Sufficient study be performed of the published literature, plant practice, and/or mechanistic behavior to establish the practical limits of water quality which can be achieved by tailings-pond type treatments.

5. Long-term programs be supported to establish what levels of heavy metals in water are hazardous to man and aquatic life.

6. New developments in metallurgical processing be assessed in terms of water requirements and waste water generation and that new process developments be supported which use less water or produce recyclable or zero discharges of waste water.

7. A more intensive study be conducted to obtain data on individual unit process waste sources. Such a study should include some provision for sampling and analysis. This work should be aimed at defining point sources, characteristics, volumes, unit waste loads and the effectiveness of treatment practices in more detail than the current study has shown to be presently available.

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## SECTION III

## INTRODUCTION

The purposes of this study are to assess current water-pollution-control practices and problems and to provide a basis for recommending specific directions to develop water-pollution-control methods in the nonferrous metals industry. The approach used in this study and in this report has been to deal with specific practices and problems rather than with generalities or overall considerations. This study, in attempting to be specific, has thus dealt with the variegated and individualistic nature of the metal-producing operations which constitute the total industry.

This report is organized to present the data obtained in groupings which are determined by the relationships between production operations. Thus, Volume I deals with the production processes and water-use practices of the copper, lead, and zinc industries. These major metal-plant operations include the manufacture of the following by-products: cadmium; "by-product" gold, silver, platinum, palladium, and rhodium; arsenic; bismuth; thallium, indium, selenium, tellurium, and molybdenum concentrates or oxides; antimony; and the metal compounds arsenic trioxide, copper sulfate, nickel sulfate, zinc oxide, zinc sulfate, and sulfuric acid. Volume II deals with operations producing alumina and aluminum, mercury, primary gold and silver, and molybdenum and tungsten.

In preparing this report, it was found necessary to deal with manufacturing processes in a somewhat intensive manner in order to identify the process steps which produce characteristic components of waste water; i.e., in some cases the primary metal product is so efficiently extracted that little waste is generated, while in other cases, marginal amounts of material from by-product operations or nominally minor components of raw materials appear in waste streams.

The method used in the study was to assemble the often fragmentary information available in the literature and, more importantly, to obtain information directly from the industry. The letters of inquiry sent to selected companies requested information on current practices of water usage and on the sources, characteristics, and amounts of waste water, as well as the industry's own statements of problem areas and treatment needs. Two constraints were placed on the data supplied by industry: that such information be supplied voluntarily and at the expense of industry, and that the specific sources of each lot of information remain anonymous.

In reporting the results of this study, separate sections have been devoted to each metal or metal grouping. Each section discusses the

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size and distribution of the particular industry, its economic characteristics, the technology employed, its water-usage characteristics, its waste-collection, -treatment, and -disposal practices, and anticipated future treatment requirements.

## SECTION IV

## PROCEDURES

The sequence of tasks in this program consisted of:

1. Compilation of a list of the companies and plant facilities in the United States which produce nonferrous metals

2. Contacting the identified companies by telephone, letter, or personal visits to obtain the desired information

3. Compilation and analysis of the data obtained to prepare this report

4. Use of documentary sources wherever available to obtain required associated information such as industry structure, overall economic aspects, process technology, prior studies on water usage, and other supplementary information.

The open literature was found to contain little specific information on water problems or treatment in the nonferrous-metals industry. This study, therefore, placed its main reliance for specific details on the voluntary contributions of unpublished data from industry. Further, it was found that the degree of precise knowledge of plant water usage is still highly variable from plant to plant.

Out of 56 companies approached, about 50 percent responded by submitting data in varying degrees of detail. Their replies covered 78 facilities ranging from single mine operations to complexes of mines, mills, smelters, refineries, etc. The responses received provided information on 35 mines, 33 concentrators, 8 copper leach-precipitation operations, 27 copper, lead, and zinc smelters, 20 refineries, 8 sulfuric acid plants, and 8 power plants.

In view of the extreme complexity of the nonferrous-metals industry and recognizing that many who use this report may be unfamiliar with the industry, it was decided that each section should include a more or less detailed description of the industrial segment, its structure, and technology as a convenient aid to understanding and interpreting its water- and waste-treatment problems and practices.

# SECTION V

## THE PRIMARY COPPER INDUSTRY

### Major Characteristics

The primary copper industry is a vast network of mines and treatment facilities spread over 19 states in the country, producing annually about 1.7 million tons of refined copper. The unit operations required to produce this copper, aside from exploration or development, are mining, physical concentration of ores, smelting, and refining. In the case of some ores not amenable to physical concentration, either technically or economically, auxiliary processes such as leaching, cementation, solvent extraction, and electrowinning are also employed. Although these processes will be described in detail later in this report, brief definitions of them are presented at this time to assist the reader in understanding the intervening tables and texts.

| | |
|---|---|
| Exploration | -- Locating, outlining, and evaluating ore bodies. |
| Development | -- Preparing the ore body for mining, as by removing overburden, sinking shafts, driving tunnels, etc. |
| Mining | -- Removal of the ore from open-pit or underground mines. |
| Concentration | -- Copper ores typically containing from about 0.6 to about 1.5 to 2.0 percent copper yield over 90 percent of the copper produced. These are concentrated by the relatively cheap physical concentration process of flotation, to eliminate the valueless material and produce a "concentrate" containing 15 to 35 percent copper which can then be further processed. |
| Smelting | -- A high-temperature series of furnacing operations in which copper concentrates produced from concentrating ores, together with relatively small quantities of higher grade ore and other copper products, are converted to a partially refined copper. |
| Refineries | -- There are two types of refineries--electrolytic and "fire" refineries. The purpose of refining is to produce copper of acceptable physical, chemical, and electrical properties for subsequent fabrication into finished products. Most copper is refined electrolytically. |
| Leaching | -- Some ores are too low in grade or of such mineralogical composition that they cannot be economically treated |

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even by the relatively cheap flotation process. These are "leached", that is, subjected to treatment by dilute sulfuric acid solution, whereby copper is dissolved for subsequent recovery by specialized methods such as cementation, solvent extraction, electrowinning, etc.

## Geographical Distribution

The distribution of copper-producing facilities throughout the United States is shown in Figure 1.

### Mines

Table 1 is a state-by-state breakdown of the various types of mines producing copper in the United States for the year 1969 and the amount produced in that year.(1,2,3) For comparison, preliminary figures for 1970 are included. The table shows, for each of the states producing copper, the number of mines in operation and the tonnages of copper they produced. The table also shows the number of leaching installations in the various states and the tonnage produced by them in 1969.

As shown in the table, the "copper" mines, i.e., those operated primarily for their copper value, produced, in 1969, about 1.3 million tons of recoverable copper out of a total production for that year of about 1.55 million tons, or more than 80 percent. Except for one large mine in Michigan and five relatively small mines in Tennessee, the "copper" mines are located in the West and Southwest in the states of Arizona, Montana, Nevada, New Mexico, and Utah.

The next major contributors to copper production are the various leaching cleanup and recovery operations which accounted, in 1969, for about 170,000 tons of copper or about 10 percent of total production. Many of these and most of the tonnage they produced are associated with copper-mining operations, which customarily leach low-grade and oxidic ores.

Copper production from the by-product mines (copper-lead-zinc, tungsten, iron, and precious metals), while economically important, is relatively small.

Major copper mines, their location, and approximate production data are shown in Table 2.

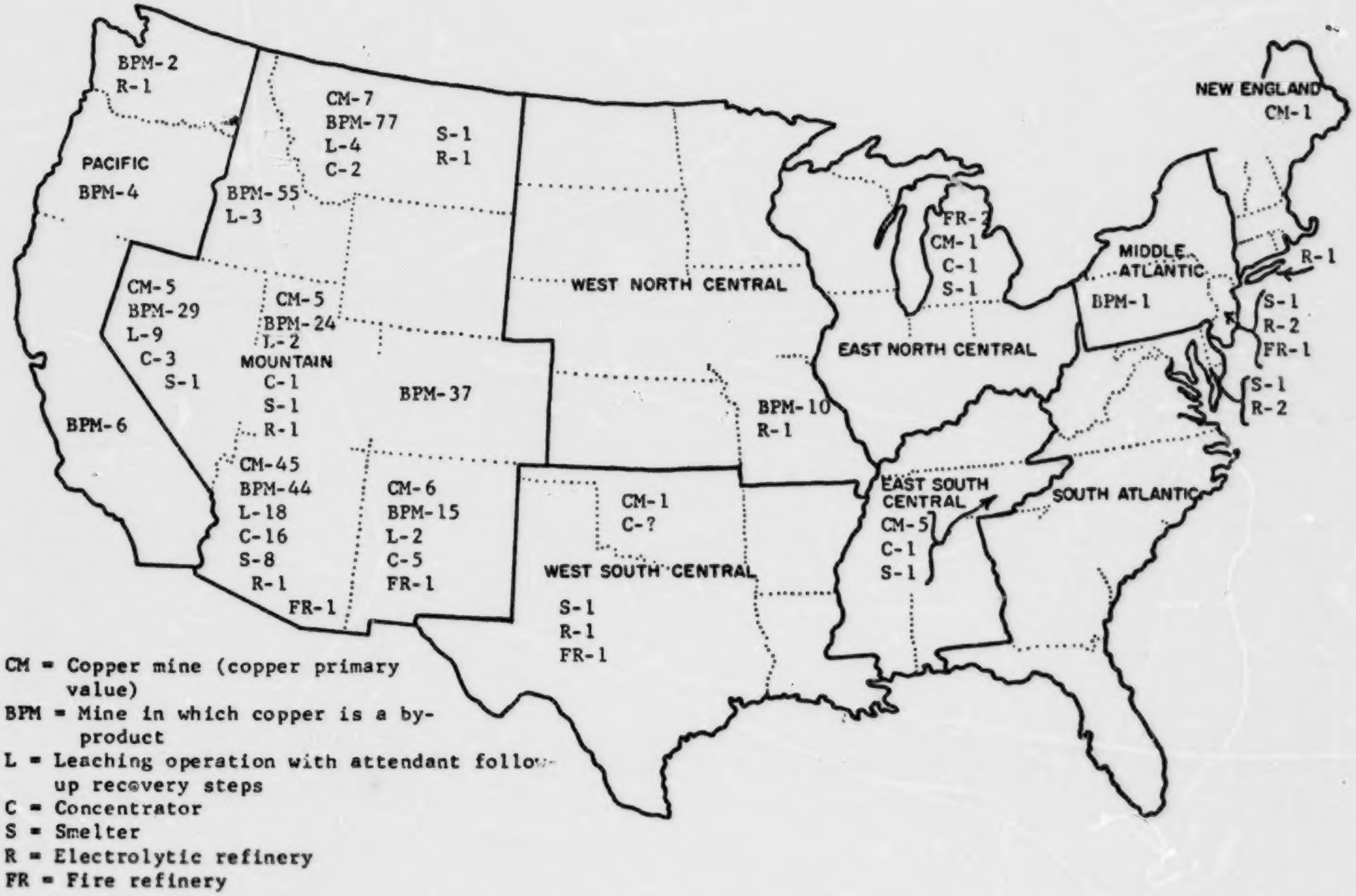

FIGURE 1. GEOGRAPHICAL DISTRIBUTION OF PRIMARY COPPER PRODUCTION FACILITIES IN THE UNITED STATES

TABLE 1. MINE PRODUCTION OF COPPER IN THE UNITED STATES[(a)]

| State | From Copper Mines |  | From Copper-Lead-Zinc Mines |  | From Lead-Zinc Mines |  | From Tungsten Mines |  | From Iron Mines |  | From Leaching, Cleanup, etc. |  | From Gold-Silver Mines |  | Total Production[(c)], short tons |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | No. of Mines | Production, short tons | No. of Mines | Production, short tons | No. of Mines | Production, short tons | No. of Mines | Production, short tons | No. of Mines | Production, short tons | No. of Facilities | Production, short tons | No. of Mines | Production, short tons | 1969 | 1970 |
| Arizona | 45[(b)] | 738,760 | 3 | 3,216 | 8 | minor |  |  |  |  | 18 | 58,517 | 33 | 869 | 801,363 | 910,000 |
| California[(b)] |  |  |  |  |  |  | 1 | 1000 |  |  |  |  | 5 | minor | 1,129 | 700 |
| Colorado |  |  | 4 | 2,695 | 28 | 789 |  |  |  |  |  |  | 5 | 113 | 3,598 | 3,820 |
| Idaho |  |  | 11 | 45 | 32 | 557 |  |  |  |  | 3 | 50 | 12 | 2,481 | 3,332 | 3,577 |
| Maine |  |  | 1 | minor |  |  |  |  |  |  |  |  |  |  | (a) | (a) |
| Michigan | 1 | 75,226 |  |  |  |  |  |  |  |  |  |  |  |  | 75,226 | 69,500 |
| Missouri |  |  |  |  | 10 | 12,664 |  |  |  |  |  |  |  |  | 12,664 | 11,282 |
| Montana | 7 | 90,538 |  |  | 20 | 10 |  |  |  |  | 4 | 12,664 | 57 | 125 | 103,314 | 123,031 |
| Nevada | 5 | 100,671 |  |  | 10 | 64 |  |  |  |  | 9 | 4,163 | 19 | 27 | 104,924 | 101,000 |
| New Mexico[(b)] | 6 | 51,289[(b)] | 4 | 1,100 | 4 | 157[(b)] |  |  |  |  | 2 | 38,218[(b)] | 7 | minor | 119,956 | 165,260 |
| Oklahoma | 1 | minor |  |  |  |  |  |  |  |  |  |  |  |  | (d) | (d) |
| Oregon |  |  |  |  |  |  |  |  |  |  |  |  | 4 | minor | (d) | (d) |
| Pennsylvania |  |  |  |  |  |  |  |  | 1 | 3,382 |  |  |  |  | 3,382 | 2,538 |
| Tennessee | 5 | 15,353 |  |  |  |  |  |  |  |  | 2 | 57,048 | 4 | 485 | 15,353 | 15,000 |
| Utah | 5 | 236,720 | 1 | 1,032 | 19 | 1,412 |  |  |  |  | 2 | 57,048 | 4 | 485 | 296,699 | 295,000 |
| Washington |  |  |  |  | 2 | minor |  |  |  |  |  |  |  |  | (d) | (d) |
| Other |  |  |  |  |  |  |  |  |  |  |  |  |  |  | 3,621 | 5,142 |
| Total | 75 |  | 24 |  | 133 |  | 1 |  | 1 |  | 38 |  | 146 |  | 1,544,579 | 1,705,900 |

(a) 1969 U. S. Bureau of Mines Data except where otherwise noted. (1)

(b) 1968 U. S. Bureau of Mines Data. (2)

(c) Data from Copper Development Association. (3)

(d) Included in "other".

(e) 16 Major copper mines in Arizona account for over 95 percent of the state's production.

TABLE 2. MAJOR COPPER-PRODUCING MINES IN THE UNITED STATES(4,5)

| Mine | Location | Company | Type | Tonnage (ore) |
|---|---|---|---|---|
| | | **Arizona** | | |
| Bagdad | Bagdad | Bagdad Copper Corp. | Open pit | 2,100,000 |
| Christmas | Near Winklemen | Inspiration Consolidated | Open pit | |
| Copper Queen | Bisbee | Phelps Dodge | Underground | 6 to 7,000,000 |
| Esperanza | Sahuarita | Duval Corporation | Open pit | 5,480,000 |
| Inspiration | Inspiration | Inspiration Consolidated | Open pit | 5 to 6,000,000 |
| Lavender Pit | Bisbee | Phelps Dodge | Open pit | 6 to 7,000,000 |
| Magma | Superior | Magma Copper | Underground | 45,000 |
| Castle Dome | Miami | Cities Service | Leaching | |
| Copper Cities | Miami | Cities Service | Open pit | 4,000,000 |
| Mineral Park | Kingman | Duval Corporation | Open pit | 6,200,000 |
| Mission | Sahuarita | American Smelting & Refining | Open pit | 8,000,000 |
| Morenci | Morenci | Phelps Dodge | Open pit | 19,000,000 |
| New Cornelia | Ajo | Phelps Dodge | Open pit | 11,000,000 |
| Pima | Pima | Pima Mining Company | Open pit | 13,000,000 |
| Ray Pit | Hayden | Kennecott Copper | Open pit | 12,000,000 |
| San Manuel | San Manuel | Magma Copper Company | Underground | 14,000,000 |
| Sierrita | Sahuarita | Duval Corporation | Open pit | 20,000,000 |
| Silver Bell | Silver Bell | American Smelting & Refining | Open pit | |
| Twin Buttes | Anaconda | Anaconda | Open pit | 10,000,000 |
| | | **Michigan** | | |
| White Pine | Ontanagon Co. | Copper Range Co. | | ca 6,000,000 |

Continued on following page.

TABLE 2. MAJOR COPPER-PRODUCING MINES IN THE UNITED STATES (continued)

| Mine | Location | Company | Type | Tonnage (ore) |
|---|---|---|---|---|
| | | **Montana** | | |
| Butte | Butte | Anaconda | Underground | ca 10,000,000 |
| Berkely Pit | Silver Bow | " | Open pit | " |
| Mountain Con | Butte | " | Underground | " |
| Leonard | " | " | " | " |
| Belmont | " | " | " | " |
| Steward | " | " | " | " |
| Kelley | " | " | " | " |
| | | **Nevada** | | |
| Liberty Pit | Ely | Kennecott Copper Corp. | Open pit | |
| Yerington | Weed Heights | Anaconda | Open pit leaching | 2,000,000 |
| Veteran | Ely | " | -- | -- |
| Copper Canyon | | Duval Corporation | -- | -- |
| Ruth | | Anaconda | Underground | -- |
| | | **New Mexico** | | |
| Chino | Santa Rita | Kennecott | Open pit | 8,000,000 |
| Tyrone | Silver City | Phelps Dodge | Underground | Undetermined |
| Misens Chest Group | Lordsburg | Banner | Underground | Undetermined |
| | | **Tennessee** | | |
| Copperhill Group | Copperhill | Cities Service | Underground | 2,000,000 |
| | | **Utah** | | |
| Utah Copper | Bingham | Kennecott Copper | Open pit | 40,000,000 |

### Concentrators

Concentrating facilities shown in Figure 1 refer only to the copper mines and not to the mines in which copper is a by-product. As explained previously, water problems associated with the by-product mines are properly chargeable to other segments of the nonferrous-metal-production industries.

It will be noted that the number of concentrators shown for the copper mines in the major producing states are considerably less than the number of copper mines (Montana, Nevada, Utah, Arizona, New Mexico). This is because one concentrator may serve a number of mines.

### Smelters

The location by states and capacities of smelters and refineries are shown in Table 3.

## Contribution to the United States Economy

Up-to-date data to illustrate the direct importance of the primary copper industry to the United States economy were not available at the time of this study. The latest information, for 1967 which was unfortunately a strike year, will provide some idea of the magnitude of this contribution. These data, selected from the 1967 Census of Manufactures(6), are shown in Table 4.

### Future Development of the Industry

Projections of the growth rate of the copper industry have been published in various terms. One such projection predicts an increase in consumption of 4-1/2 to 5 percent during the 1970 to 1975 period.(7) This prediction, in terms of total consumption, gives a rate higher than the predicted rate of expansion of the general economy. However, the fact that the prediction is in terms of consumption makes it hard to apply to considerations of domestic primary-plant operations (i.e., water use) since consumption includes imports of raw material and finished products, and production from secondary materials.

A prediction published by the Bureau of Mines is given in terms of metal content of domestically mined ores and would be considered a better indicator of the possible expansion of plants within the United States. This prediction is based on 1968 production data, and gives

TABLE 3. COPPER SMELTERS AND REFINERIES

| | | Smelters | | Electrolytic Refineries | | Fire Refineries | |
|---|---|---|---|---|---|---|---|
| State | City | Company | Annual Capacity[(a)], s.t. of charge | Company | Annual Capacity[(a)], s.t. of charge | Company | Annual Capacity, tons of product |
| Arizona | Hayden | A S and R [(c)] | 360,000 | | | | |
| | Hayden | Kennecott | 400,000 | | | | |
| | Miami | Inspiration | 360,000 | Inspiration | 63,000 | | |
| | Superior | Magma | 150,000 | | | | |
| | San Manuel | Magma | 360,000 | | | | |
| | Morenci | Phelps Dodge | 900,000 | | | | |
| | Ajo | Phelps Dodge | 300,000 | | | | |
| | Douglas | Phelps Dodge | 1,250,000 | | | | |
| Maryland | Ann Arundel | | | Kennecott | 198,000 | | |
| | Baltimore | | | A S and R[(c)] | 198,000 | | |
| Michigan | White Pine | White Pine | 65,000[(b)] | | | White Pine | 65,000 |
| | Hancock | Quincy | 12,000[(b)] | | | Quincy | 12,000 |
| Missouri | St. Louis | | | Cerro | 42,000 | | |
| Montana | Anaconda | Anaconda | 1,000,000 | | | | |
| | Great Falls | | | Anaconda | 150,000 | | |
| Nevada | McGill | Nevada | 440,000 | | | | |
| New Jersey | Carteret | | | U.S. Metals | 150,000 | U.S. Metals | 125,000 |
| | Perth Amboy | | | A S and R | 168,000 | | |
| | Raritan | | | International Smelting | 240,000 | | |
| New Mexico | Hurley | Kennecott | 400,000 | | | Kennecott | 84,000 |
| Texas | El Paso | A S and R | 420,000 | Phelps Dodge | 290,000 | Phelps Dodge | 25,000 |
| Utah | Garfield | Kennecott | 1,225,000 | Kennecott | 204,000 | | |

(a) Data from U. S. Bureau of Mines Information Circular 8225, published in 1965.

(b) Production capacity.

(c) A S and R = American Smelting and Refining., Inc.

### TABLE 4. SELECTED ECONOMIC STATISTICS FOR THE PRIMARY COPPER INDUSTRY (1967)(6)

| Characteristics | Copper Ores | Smelting and Refining |
|---|---|---|
| Number of establishments | | |
| Total | 157 | 32 |
| With 20 employees or more | 61 | 32 |
| Number of employees | 21,000 | 11,600 |
| Payroll, millions of dollars | 170.9 | 80.6 |
| Value of shipments, millions of dollars | 675.9 | 1184.1 |
| Capital expenditures, millions of dollars | 123.6 | 51.7 |
| Materials consumed: | | |
| Ores, concentrates, precipitates, short tons | -- | 3,601,500 |
| Other forms of copper metal, short tons | -- | 435,700 |
| Delivered cost, millions of dollars | | 827.6 |
| Cost of all other materials and supplies, millions of dollars | | 77.2 |
| Cost of purchased fuels and electrical energy, millions of dollars | | 21.5 |
| Product made by primary copper refiners, short tons | | 1,307,900 |

an estimate up to the year 2000 with a range of possible growth rates from a low of 3.7 percent to a high of 5.2 percent.(8) The production portion of this estimate is shown in Figure 2, along with past production figures. The estimated expansion of primary mine production is shown as related to past mine production. The figure also illustrates that primary refinery production, while related to domestic mine production, shows the inclusion of domestic and/or imported raw materials and scrap in primary refinery production. The estimated primary domestic mine production for the year 2000, ranging from 3.8 to 6.1 million tons of copper, is coupled, in the published prediction, with an estimated demand for primary copper of 4.9 to 7.8 million tons, with the difference again being attributable to imports.

## Raw Materials

The major raw material in the primary copper industry is, of course, the ore. In 1970, for example, over 300 million tons of ore were mined to produce 1.7 million tons of copper. Other raw or auxiliary materials going into the production of refined copper are as follows:

Mining -- blasting materials, fuels, timber

Transportation -- fuels, lubricants

Concentration -- various conditioning chemicals (such as zinc sulfate, lime, sodium sulfide, cyanide); flotation reagents (such as xanthates, phosphates, oils, and frothing agents); chemicals for improving flocculating, settling, and filterability (such as various proprietary compounds, lime)

Smelting -- fluxing materials such as quartz rock, silicate ores, lime rock, fuels (coal, coke, natural gas, oil)

Fire Refining -- various fuels, purification gases such as air, oxygen, and natural gas

Electrolytic Refining -- sulfuric acid, various addition agents, such as glue, etc., to improve deposition

Machinery -- a high capital investment is made in specialized machinery such as drilling and earth-moving machines and other plant equipment, e.g., furnaces.

There are about 160 known copper minerals in nature. Only about a dozen of these are commercially important and 5 or 6 account for over 90 percent of the copper produced. The minerals of importance in United States ores are shown in Table 5.

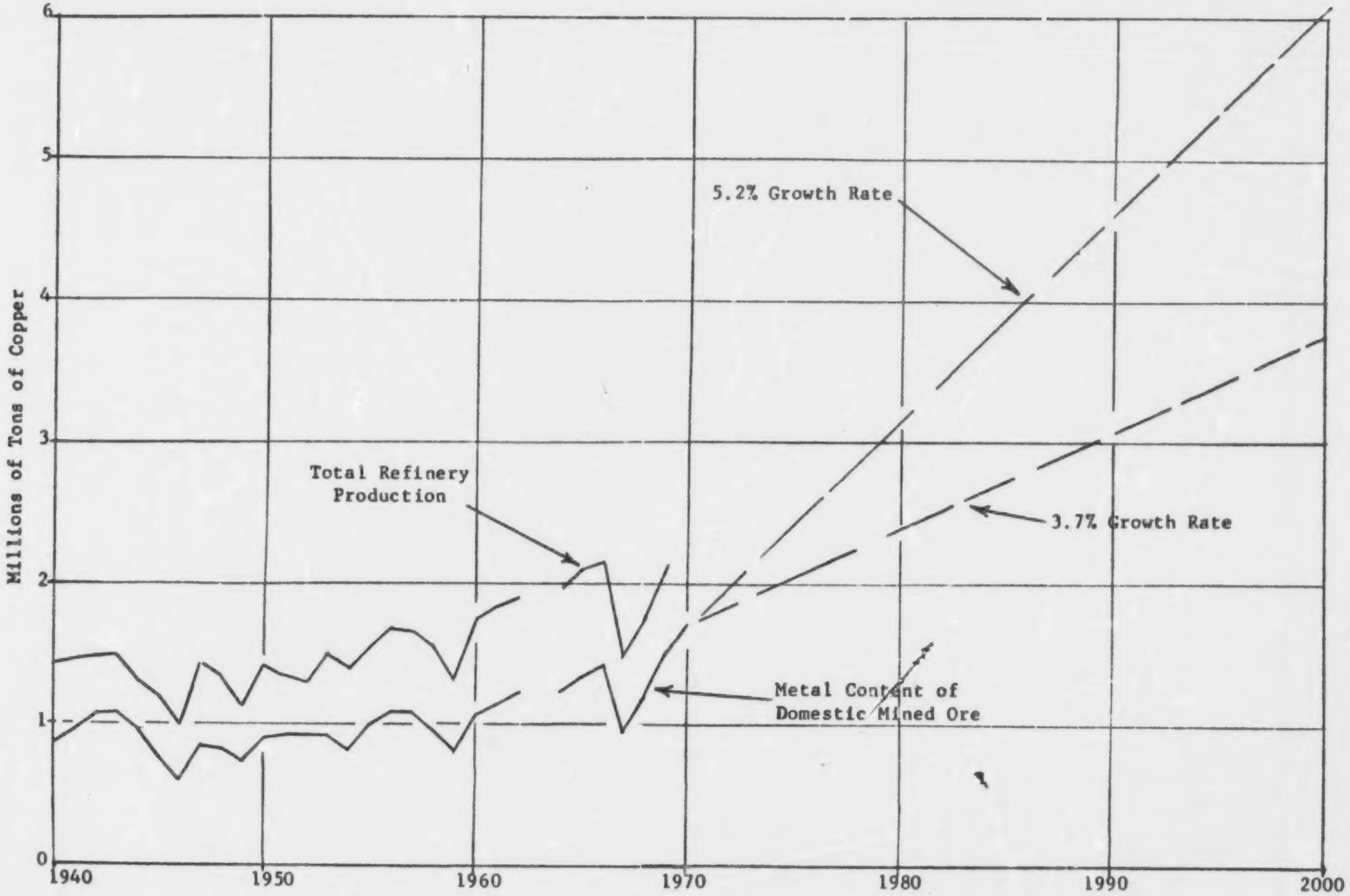

FIGURE 2. PAST PRODUCTION AND ESTIMATED GROWTH OF THE PRIMARY COPPER INDUSTRY

TABLE 5. COPPER MINERALS IMPORTANT IN U.S. PRODUCTION(4)

| Mineral | Composition | Copper Content of the Mineral Form, percent |
|---|---|---|
| Native copper metal | Cu | 100 |
| | Sulfide Ores | |
| Chalcopyrite | $CuFeS_2$ | 35 |
| Chalcocite | $Cu_2S$ | 80 |
| Covellite | CuS | 66 |
| Bornite | $Cu_5FeS_4$ | 63 |
| Enargite | $Cu_3As_5S_4$ | 48 |
| | Oxide Ores | |
| Cuprite | $Cu_2O$ | 89 |
| Malachite | $CuCO_3 \cdot Cu(OH)_2$ | 57 |
| Azurite | $2CuCO_3 \cdot Cu(OH)_2$ | 55 |
| Chrysocolla | $CuSiO_3 \cdot 2H_2O$ | 36 |

These minerals occur in a variety of modes to make up what is called "ore", that is, a deposit which can be mined at a profit. Rarely in the United States are they found in any quantity as massive deposits of the pure mineral that can be mined selectively and smelted, but are practically always dilute mixtures with other rocks of little or no value. The most important copper-ore type in the United States is the so-called "porphyry" copper deposits. These are extensive masses of rock throughout which crystals of various copper minerals are more or less uniformly disseminated, and which, although low grade, may profitably be mined on a massive nonselective scale. The copper minerals generally associated with the porphyries are the various oxides, such as cuprite and malachite which have been converted to these oxide forms by weathering processes and, lower in the deposit, various sulfide minerals such as chalcocite, covellite, and chalcopyrite. The porphyry copper deposits account for the major portion of copper production. The average grade of ore for all copper production in 1968 was 0.6 percent. The copper content of the porphyry ores, therefore, must lie around 0.6 percent. Porphyry ores are mined by open-pit methods.

Other major types of ore are the vein, pipe, and bedded deposits, which generally yield higher grade ores ranging from 3 to about 10 percent copper, and which are usually mined by underground methods. The copper minerals in such deposits are sulfidic, frequently associated with sulfides of other metals such as pyrite or pyrrhotite and include chalcopyrite, bornite, chalcocite, and covellite. A few of the deep United States copper deposits contain some copper-arsenic minerals such as enargite or tennantite.

Native copper may occur in unimportant quantities in oxidized ore deposits, but in one place in the United States (Michigan) it is a significant ore mineral associated with covellite, a copper sulfide. Minor, though economically important, concentrations of copper, generally as sulfide but occasionally as an oxidic material, also are found with the ores of other metals (lead, zinc, silver, iron).

The copper ores of the United States may be classified as follows:

(a) Concentrating-grade ores. As mined, these will contain from about 0.6 to about 1 or more percent copper mostly as sulfide. They account for about 75 to 80 percent of primary copper production in the country. The so-called porphyry coppers of the west, mined by open-pit methods, are the most important typical sulfide ores of concentrating grade. Underground mines also produce such ores. These ores may also contain oxidic copper in minor proportions.

(b) Low-grade (or leaching grade) ores. These are the ores containing significant quantities of copper as sulfide and/or oxide and which cannot be economically concentrated by the basic process. They may contain from a few tenths to about 0.5 percent copper. In mining, such ores are segregated and leached. They occur near the top and to some extent throughout copper deposits, and in the course of mining must be removed so that the higher grade ore can be mined systematically and economically.

(c) High-grade sulfide ores. These are generally obtained from underground operations and occur in vein, pipe, and bedded deposits. They may range from about 3 to 10 percent copper in the United States. Their tonnage is not great.

(d) Mixed sulfide-oxide ores. These are ores in which the sulfides and oxide minerals are present in approximately equal amounts, and which require special treatment to yield an economic level of recovery. Such ores may range in grade from about 0.6 to 2 percent copper, with the bulk of them being below 1 percent.

(e) Native copper ores. The only important deposits containing native copper ores occur in Michigan. As mined, they contain about 1 percent of copper, generally associated with some silver.

(f) In a few locations, and generally on a small scale, copper may occur largely or altogether in oxide minerals, such as chrysocolla, malachite, or azurite. Such ores are generally treated by leaching methods.

(g) Ores of other metals, notably lead and zinc, but also silver, molybdenum, tungsten, and iron, may yield copper as a by-product. As discussed previously, little emphasis will be placed on such ores or their treatment in this section of the report.

Most of the copper sulfide ores mined in the United States contain gold and silver in small but economically significant concentrations. These are recoverable as such in the conventional smelting-electrolytic refining process, but not in most processes involving leaching or fire refining. The sulfide copper ores often contain molybdenum in important amounts which can be readily recovered in normal concentration operations.

## Major Process Operations

Figure 3 is a graphic description of the basic copper process which accounts for virtually all of the copper produced in the United States. About 80 percent of the copper ores mined in the country go through all stages of the process shown, from mining and concentration through electrolytic refining. Amost all of the remaining 20 percent of the copper in ores treated by other processes is merely preconcentrated by these other processes and at some stage or other is introduced into the basic process for eventual conversion into refined copper. Minor amounts of primary copper are produced strictly by hydrometallurgical methods.

Figure 4 is a flowsheet of the primary copper industry from ore to refined copper. The figure shows the various types of ores and the processing or handling steps that are involved in treating the variety of ore grades and types encountered and illustrates the relationship of these auxiliary processes to the basic process.

In the figure, the materials and processing steps are numbered. These numbers are keyed in with the subsequent text in which pertinent explanations and details are presented.

As shown in Figure 4, there are seven indicated routes (Roman numerals) to copper production, depending largely on the grade and type of ore. Route I, which accounts for the production of over 90 percent of the primary copper produced in the United States, is shown at the extreme left side of the figure. This is the basic process of concentration, smelting, and refining depicted in Figure 3. In most of the other routes, some product, at some stage in the process, will be sent to some stage of the basic process.

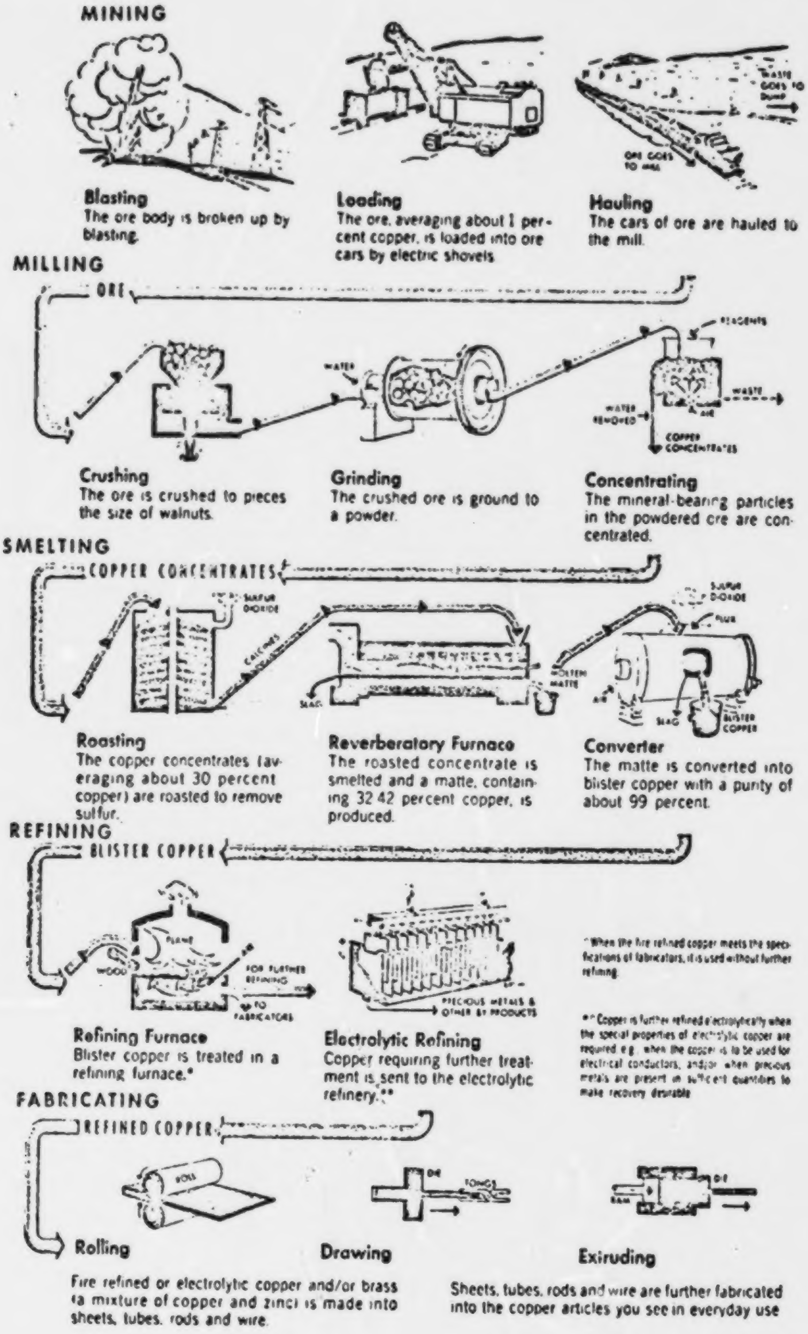
MINING
Blasting
The ore body is broken up by blasting.
Loading
The ore, averaging about 1 percent copper, is loaded into ore cars by electric shovels.
Hauling
The cars of ore are hauled to the mill.
WASTE GOES TO DUMP
ORE GOES TO MILL
MILLING
ORE
WATER
REAGENTS
WASTE
WATER REMOVED
AIR
COPPER CONCENTRATES
Crushing
The ore is crushed to pieces the size of walnuts.
Grinding
The crushed ore is ground to a powder.
Concentrating
The mineral-bearing particles in the powdered ore are concentrated.
SMELTING
COPPER CONCENTRATES
SULFUR DIOXIDE
CALCINES
SLAG
MOLTEN MATTE
FLUX
AIR
BLISTER COPPER
Roasting
The copper concentrates (averaging about 30 percent copper) are roasted to remove sulfur.
Reverberatory Furnace
The roasted concentrate is smelted and a matte, containing 32-42 percent copper, is produced.
Converter
The matte is converted into blister copper with a purity of about 99 percent.
REFINING
BLISTER COPPER
FLAME
WOOD
FOR FURTHER REFINING
TO FABRICATORS
PRECIOUS METALS & OTHER BY-PRODUCTS
Refining Furnace
Blister copper is treated in a refining furnace.*
Electrolytic Refining
Copper requiring further treatment is sent to the electrolytic refinery.**
*When the fire refined copper meets the specifications of fabricators, it is used without further refining.
**Copper is further refined electrolytically when the special properties of electrolytic copper are required, e.g., when the copper is to be used for electrical conductors, and/or when precious metals are present in sufficient quantities to make recovery desirable.
FABRICATING
REFINED COPPER
ROLLS
DIE
TONGS
RAM
DIE
Rolling
Drawing
Extruding
Fire refined or electrolytic copper and/or brass (a mixture of copper and zinc) is made into sheets, tubes, rods and wire.
Sheets, tubes, rods and wire are further fabricated into the copper articles you see in everyday use.

FIGURE 3. BASIC STEPS--COPPER ORE TO FINISHED PRODUCT(4)

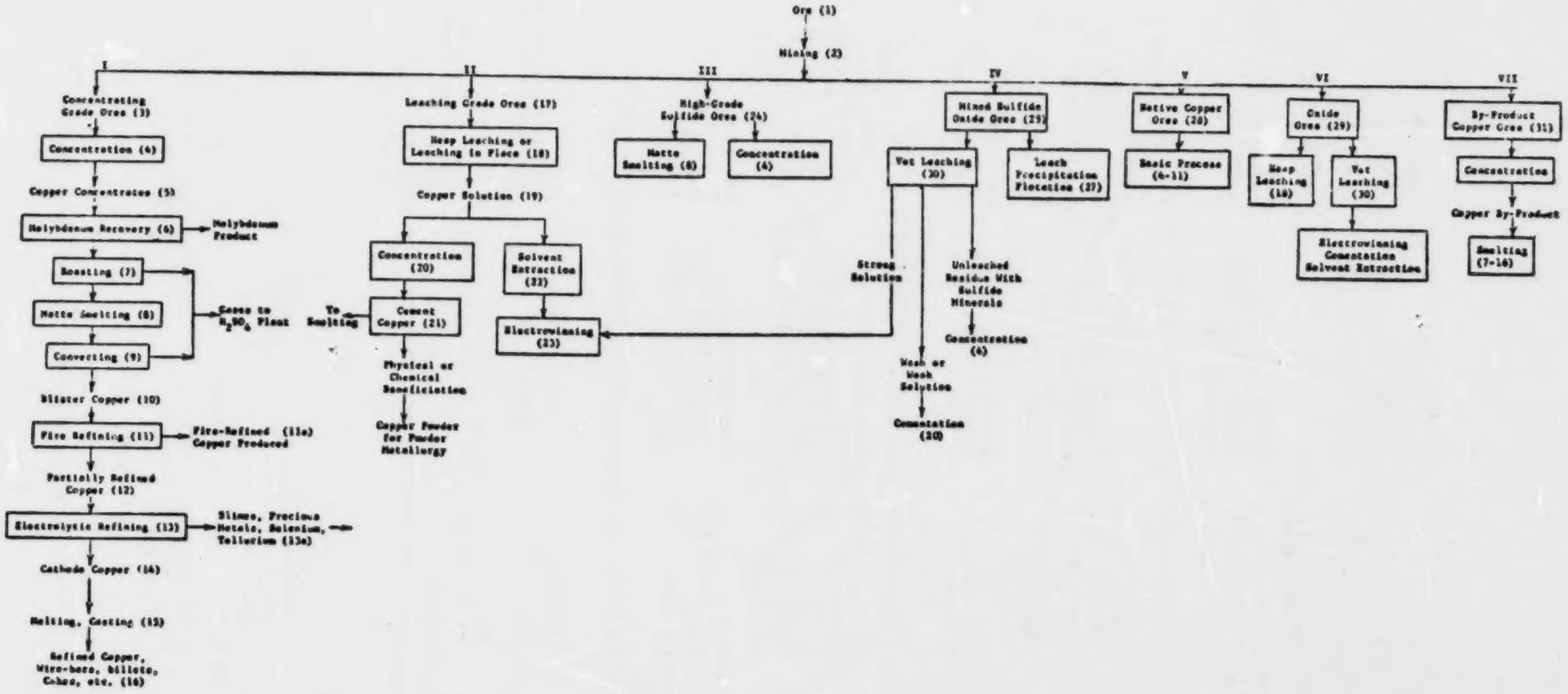

FIGURE 4. DIAGRAM OF OPERATIONS IN COPPER PRODUCTION

## Mining

There are three principal mining methods used in the copper industry: open pit, caving, and stoping.

The choice of mining method depends on many factors, mostly associated one way or the other with economics. They include such considerations as size, configuration, and grade of the ore body, its depth below the surface, topography, climate, accessibility, etc.

Open Pit. Open-pit mining, as its name implies, involves the removal of ore from deposits at or near the surface, by a cycle of operations consisting of drilling blast holes, blasting the ore, loading the broken ore onto railroad cars or trucks, and transporting it to the concentrators. In a few cases, blasting is not required and the ore is "ripped" by bulldozers prior to loading. Before a given deposit can be worked by open-pit methods, barren surface rock or earth must be removed to uncover the ore body. This can be a major operation. In a mine now being developed in Arizona, as much as 500 feet or more of overburden was removed before systematic mining could be begun.

In addition to the barren overburden or waste rock, it is also necessary, in open-pit mining, to remove low-grade copper ores from the top or throughout the ore body so that mining of the concentrating-grade ore can proceed systematically and with optimum efficiency. As a rule of thumb, concentrating-grade ore in large open-pit mines contains about 0.6 to 1 percent of copper in a form recoverable by concentration. Significant proportions of low-grade ore, containing from 0.2 to about 0.5 percent of copper are encountered in open-pit mining. Such low-grade ore, containing oxide and/or sulfide copper minerals, cannot be economically treated in a concentrator. Where in earlier years this low-grade ore was discarded to waste, it is now hauled from the mine, piled in large heaps, and subjected to leaching.

The open-pit mines in the United States account for about 80 percent of the country's copper production. Most are quite large, yielding from about 15,000 to over 100,000 tons of ore per day.

Haulage from open-pit mines to concentrators is done by truck or rail. In some cases, conveyor belts are used to transport the ore from the pit to the concentrator. Tractor-drawn scrapers are occasionally used.

Underground Mining Methods. About 20 percent of the copper ore mined in the United States comes from some form of underground operation. The most widely practiced of these is the "caving" technique in which an ore body is undercut, and the ore under natural stressess fractures, caves, and falls through vertical or nearly vertical tunnels called "raises" to loading chutes on a still lower level in the mine. Block caving is an efficient, low-cost operation, but requires homogeneous, rather weak ore bodies of more or less regular configuration for optimum results. Several large copper mines in the United States use this form of underground mining.

Another important underground mining method is the so-called "top slicing". In this method a cut is made on the top section of the ore body and the ore removed. During mining the floor of the "slice" is covered with a timber "mat". After the "slice" is mined out, the roof (overburden) is blasted and falls on the timbered floor. As successive slices are mined and caved, the overburden subsides, filling the spaces formerly occupied by ore. The mat of timbers effectively separates ore from the waste overburden and results in a less diluted ore. Although more expensive than block caving, it is preferred for the higher grade underground ore bodies.

Stoping, another method of underground mining, is the working or excavating of a deposit by methods which do not involve natural caving or caving induced by blasting. In this method, the ore body is excavated directly and the void space left after removal of the ore is filled by waste rock, tailings, etc., or the walls and roof are supported by timbering or bolting.

There are a number of stoping methods, each best adapted to the size, grade, and configuration of the ore deposit, the type and strength of the rock enclosing the deposit, etc.

## The Basic Copper Production Process
## (Items 3-16 in Figure 4, Route 1. See also Figure 3)

As previously pointed out, about 80 percent of the copper produced in United States mines is treated by the basic concentration-smelting-refining route. This involves processing copper ore containing less than 1 percent of copper which is concentrated by flotation to produce a copper concentrate containing 15 to 25 percent or perhaps more copper. These copper concentrates are smelted and refined to produce various shapes and grades of intermediate copper products.

The lineup of operations and materials shown in Column I of Figure 4 illustrates this basic process. The following sections, numerically keyed to the diagram in Figure 4, discuss these (Nos. 3 through 16).

### Concentrating-Grade Ore (3)

Concentrating-grade ore is ore containing from about 0.6 to as much as 2 percent of copper present as sulfide minerals which can be concentrated by the process later to be described. This type of ore is produced mainly by the large open-pit copper mines in the west and southwest. It consists largely of such copper minerals as chalcopyrite, chalcocite, covellite, and bornite in various combinations. Some concentrating-grade sulfide ores also may contain sulfoarsenide minerals such as enargite and tennantite. Many of the concentrating-grade sulfide ores also contain molybdenum, gold, silver, selenium, and tellurium as economically important by-products.

The nonore minerals associated with these ores, virtually valueless, cover a gamut, depending on their geological origin, and include quartz (silicon dioxide), various igneous and sedimentary silicates (feldspars, altered feldspars, clay, shale), limestone, and pyrite. These nonmetallic minerals will amount in most cases to over 95 percent by weight of the ores.

## Concentration (4)

In the United States today, concentration of copper is done by flotation. The concentration of copper ores is carried out in what are commonly called "mills". The purpose of "milling" is to recover most of the copper in the ore in a concentrate form. The basis of the flotation process by which this "concentrating" is done is as follows:

Copper sulfide minerals (and other sulfide minerals as well) possess certain surface characteristics that are quite different from those of the other minerals (silicates, quartz, etc.) present in the ore. When added to a suspension of the finely ground ore in water in small quantities, certain reagents can be made to attach themselves selectively to the surfaces of sulfide minerals. These reagents are of such a nature that, after the attachment, the surfaces of the sulfides are nonwettable and are said to be "hydrophobic" and "aerophilic". If a mixture of such sulfide and oxide minerals in water is properly treated with such reagents, and small bubbles of air are passed through the mixture, these nonwettable or aerophilic particles attach themselves to the air bubbles and, even though much denser than water, are levitated or "ballooned" to the surface.

The flotation process for copper has been developed to take full advantage of this phenomenon. It involves these basic steps.

(a) Crushing and grinding of the ore to "liberate" the copper minerals, which, in the ore itself as mined, may be completely or partially encapsulated by noncopper minerals. Crushing is done, in stages, by passing the ore through large jaw crushers and finally through gyratory or cone crushers. As mined the ore may contain boulders up to 6 feet in size. Crushing produces a final size of about 1 to 2 inches. The crushed product is then wet ground in ball mills or rod mills. These are huge cylinders containing steel balls or rods, which rotate on a horizontal axis. The crushed ore is fed with water into one end of the rotating mill, where the action of the tumbling balls or rods breaks up or "grinds" the crushed ore to the particle size required to "liberate" and/or reduce the size of the copper minerals.

The required size for flotation is always less than 35 mesh (0.016-inch diameter) which is about the maximum that can subsequently be floated effectively. Grinding to finer sizes is frequently required to obtain adequate liberation of minerals from gangue rock.

(b) Flotation. The ground mixture of ore and water is then treated with the required chemicals and passed continuously through a series of flotation cells. In copper metallurgy the required chemicals are those necessary to maintain proper pH conditions, the flotation reagents themselves which will selectively coat the copper sulfide particles, and a frothing reagent which will stabilize the froth which is formed by the passage of air bubbles to the surface. The flotation cells are rectangular tanks of various sizes and design. They are fitted with agitators which serve the dual purpose of keeping the ore particles in suspension and providing a constant supply of fine air bubbles to the cell.

As the mixture of ore and water, properly dosed, passes through a series of cells, the air bubbles collect the selectively coated copper sulfide minerals and transfer them to the froth. The froth which is being constantly produced is continuously scraped by mechanically operated paddles, and constitutes the "concentrate". The nonfloating material in the slurry constitutes the "tailings" and is discharged from the bottom of the cell. The above is a simplification to illustrate the manner in which one flotation cell would work.

In actual practices, copper mills employ literally scores, if not hundreds, of flotation cells with a wide variety of flow patterns.

Figure 5, the flowsheet of an Arizona copper mill, illustrates the complexity often encountered in flotation processing.

According to this flowsheet, the crushed ore is fed to rod mills which effect partial grinding and then to ball mills where the required degree of fineness is achieved. The ball-mill circuit is closed with wet cyclones. The cyclones are so designed that adequately ground ore is removed from the grinding circuit and sent on to flotation and insufficiently ground ore is returned to the ball mills. This avoids overgrinding and its consequent deleterious effect on the selectivity of flotation and concentrate grade. After grinding, the slurry of ore and water goes to the first stage, or rougher, flotation. Here the objective is not to obtain a high-grade finished concentrate but rather to obtain a high recovery of copper in a relatively low-grade concentrate. As shown in the diagram, the rougher flotation section in this example consists of 16 banks with 12 cells per bank. The usual practice is to feed the ore slurry into the first cell in a bank and to discharge tailings from the last cell. By this arrangement, the underflow from the first to the eleventh cell progresses to the next

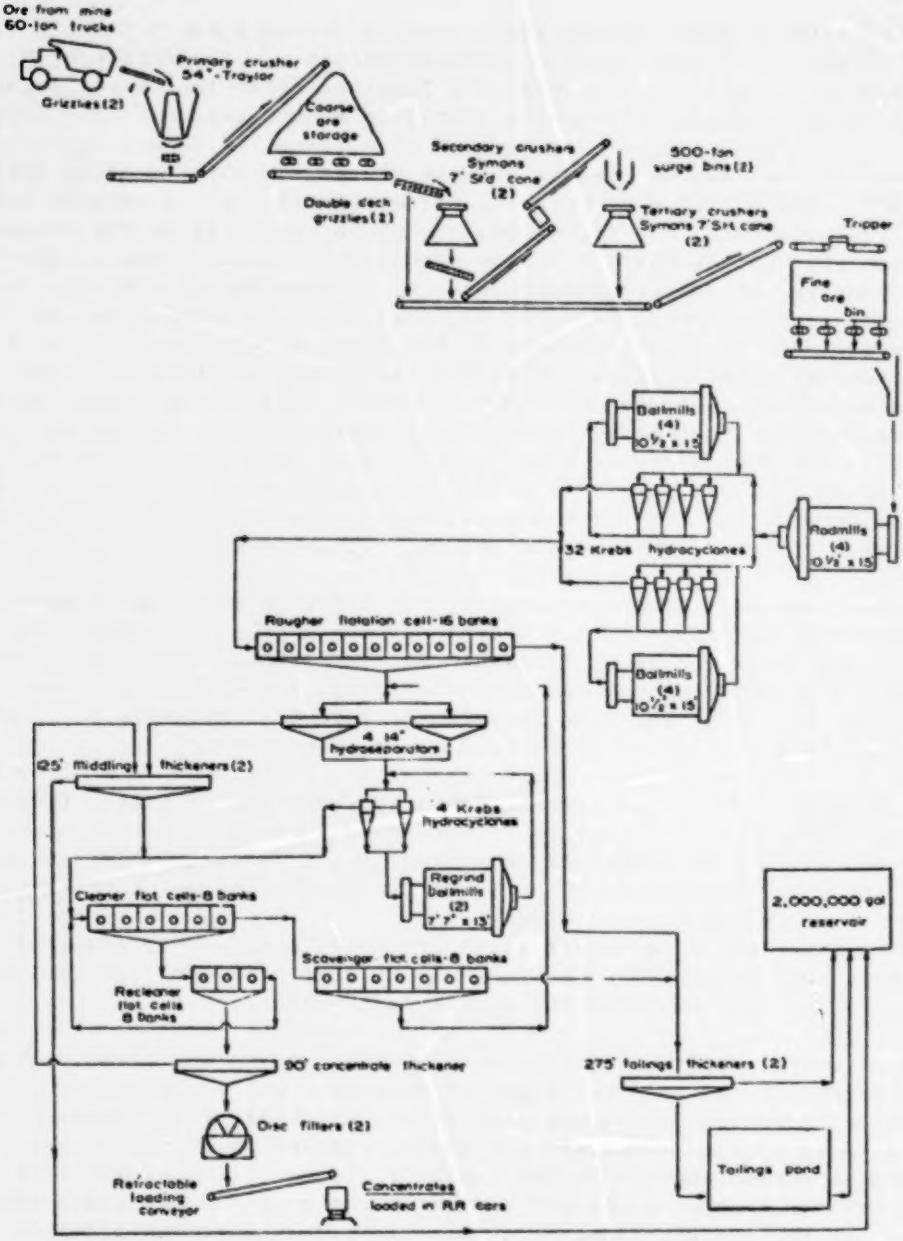

FIGURE 5. FLOWSHEET OF TYPICAL FLOTATION PROCESS[4]

cell in line, where additional time and reagent addition results in an additional copper recovery.

The combined rougher concentrates produced by scraping the froth from the rougher cells are sent to hydroseparators which effect partial separation of solids, and then to a large thickener which completes the solid separation and produces a virtually clear overflow. The solids from the hydroseparators are treated in cyclones to remove any oversize particles that may be present. These are reground in "regrind ball mills". The overflow from the cyclones in this regrind circuit joins the underflow from the thickeners and constitutes all of the rougher concentrate containing all of the recoverable copper. The rougher concentrate, which may contain about 81 percent copper, is then retreated in the "cleaner" cells. In the "cleaning" operation, generally no additional flotation reagent is required, enough remaining on the sulfide particles to ensure that they will remain floatable. The objective of the cleaning operation is to drop out the noncopper minerals by passing the pulp through banks of flotation cells similar to those used in the rougher operation. Concentrates from the cleaner cells are recleaned in a smaller but similar "recleaner" circuit. Since in recleaning some concentrate may be lost with the underflow, provisions are made to return this to the middlings thickener.

In the flowsheet shown in Figure 5, the tailings from the "cleaner" circuit are "scavenged", i.e., treated with additional reagent to recover floatable copper that escaped in the cleaning operation. Since much of the copper recovered in the scavenging operation will not be sufficiently liberated from gangue material, the scavenger tailings are returned to regrinding and subsequent cleaning and recleaning.

The copper concentrates produced are thickened and filtered, loaded into railroad cars, and sent to the smelter. The tailings produced in the operation, consisting of the underflows from the rougher and scavenging circuits, are thickened. Clear overflow from the thickener flows to a reservoir for recirculation. The thickened tailings are ponded and clear supernatant liquor from the pond is recirculated through the reservoir. Also recirculated for reuse through the reservoir is the overflow from the middlings thickener.

The flowsheet in Figure 5 should be regarded only as typical. Other concentrators employ other types of equipment and different flow patterns. Some will use spiral classifiers in place of cyclones to "close" grinding circuits. Some may not employ recleaning or scavenging. Ore tonnages, grade, and flotation characteristics of the minerals will dictate the number, size, and hookup of flotation cells, thickeners, etc. In regions where water is plentiful, recirculation of water will not necessarily be practiced.

## Copper Concentrates (5)

The concentrates produced by milling operations are always in the form of filter cake containing about 30 percent by weight of water and, on a dry basis, from about 20 to 35 percent copper. The copper content and chemical composition of concentrates will vary from mine to mine. The following tabulation lists some typical compositions of concentrates produced in Arizona mills.

Typical Copper Concentrate Compositions, percent

| Cu | Fe | S | $SiO_2$ | CaO | $Al_2O_3$ |
|---|---|---|---|---|---|
| 24.8 | 23.0 | 33.0 | 12.9 | -- | 2.5 |
| 31.3 | 22.7 | 29.8 | 14.5 | -- | 0.1 |
| 23.3 | 24.2 | 31.0 | 9.4 | 2.4 | 2.4 |
| 15.4 | 31.0 | 36.9 | 11.0 | -- | 4.3 |

## Molybdenum Recovery (6)

Many of the copper ores in the West contain molybdenum in important quantity and this valuable by-product is often recovered in concentrators. The recovery of molybdenum is described in Volume II of this report. Molybdenum in copper ores occurs as molybdenite, which is a molybdenum sulfide ($MoS_2$). This mineral is what is known as a "natural" floater and, in pure form, is so water repellant that it can be made to float in the flotation process without the use of reagents. It accompanies the copper minerals during flotation, and up to about 80 percent of the molybdenum present in the ore will report with the copper concentrates under normal conditions. In one method of molybdenum recovery, the copper concentrates are treated with lime and steam to destroy the flotation reagents which still adhere to them. The concentrates are then treated by flotation without reagents. The naturally floating molybdenum is collected, along with some copper, in a rougher concentrate, which is subsequently cleaned and recleaned. In another process, the molybdenum is separated from the copper rougher concentrates by selective flotation, cleaning, and recleaning.

## Smelting (7-8-9-10)

There are relatively few smelters in the United States and only about a dozen large mills are located close to smelters. The larger copper companies which operate mines, concentrators, and smelters ship concentrates to their own facilities. These smelters are more or less centrally located in the area of the company's mining interests and only relatively short hauls by rail or truck are necessary. Companies engaged only in mining and concentrating ship their concentrates to smelters owned by other companies.

In most cases the transportation is intrastate, but in some instances, long rail or truck hauls may be involved. Some Arizona copper mines have shipped concentrates to El Paso, Texas.

The overall purpose of smelting is to separate copper from the iron, sulfur, and gangue materials that are present in copper concentrates. The steps required include roasting, matte smelting, and converting.

## Roasting (7)

Formerly, most copper concentrates were roasted prior to smelting in the reverberatory furnace. The purposes of roasting are to dry the concentrates, eliminate sulfur to a controlled degree, and remove certain impurities such as arsenic, antimony, and selenium. At present the roasting step is frequently bypassed and new smelters have been erected which do not use roasters.

Where roasters are bypassed, drying may be accomplished by air drying or the use of mechanical equipment such as kilns. In some plants the roasting furnaces have been converted to simple driers. The elimination of sulfur in roasting is employed to control the sulfur and hence the copper concentration in the matte. Some modern concentrators are now able to control the sulfur concentration in concentrates, so that roasting is unnecessary. Many ores do not contain arsenic and antimony in quantities that must be removed prior to smelting.

In current practice, roasting is carried out either in multiple hearth furnaces or in fluidized-bed roasters. The former is a large cylindrical device up to 40 feet in height and about 20 feet in diameter containing 8 to 12 circular hearths, one above the other. A shaft carrying "rabble" arms for each hearth extends the length of the axis. As the shaft is made to rotate, "shoes" affixed to the rabble arms rake or move the concentrates over the surface of the hearth to ports discharging to the next lower hearth. These discharge ports are alternately near the circumference and at the center of the hearth, and the shoes or rakes are so set that the concentrates are moved toward the discharge port. In operating such roasters, the concentrate is charged on the top hearth and progresses downward from hearth to hearth. When additional heat is required, fuel is injected into the bottom hearth countercurrent to the flow of hot gases. Heat is provided by igniting the concentrates and passing air through the furnace. When the concentrates contain sufficient sulfur (25 percent plus), no additional fuel is required. Temperatures in this type of roaster will range from about 300 to 400 F on the top hearth to as much as 1600 to 1700 F on the bottom hearth.

## Matte Smelting (8)

Matte smelting is universally done in reverberatory furnaces. These are large roomlike structures, up to about 130 feet long and 38 feet wide, with capacities for treating up to 1500 tons of charge per day, on a continuous basis.

Figure 6 is a diagrammatic sketch illustrating the general structural and operational features of a reverberatory furnace.

The main objective of treatment in a reverberatory furnace or "matte" smelting is to collect virtually all of the copper in a molten copper-iron-sulfide material, called "matte", suitable for subsequent treatment in converters.

The feed material to the reverberatory furnace consists of the following:

(a) Copper concentrates either roasted or unroasted

(b) Possibly some high-grade copper ore

(c) Possibly some cement copper

(d) Converter slag

(e) Reagglomerated dust from smelting operations

(f) Fluxing materials, such as limestone, etc., required to form a fluid slag from silicates that may be introduced with the charge.

This feed material is added to the furnace at one end through charging ports on the roof near the side walls. As the charge enters the furnace, it collects in piles alongside the furnace walls still in a solid state. Heat is supplied by the burning of powdered coal, oil, or gas through burners placed in the end wall near the charging end of the furnace. The entire interior of the furnace is heated to temperatures ranging from about 2000 to 3000 F. Radiation of this heat from the roof and walls of the furnace causes the charge to melt and form two separate liquid phases--on the bottom a matte containing almost all of the recoverable copper as a sulfide and on top a liquid slag composed of silicates of iron and other metals introduced with the charge material. A small proportion of the total copper in the charge is also present in the slag.

The molten matte and slag flow to the discharge end of the furnace and are tapped off into ladles. The slag is discarded to waste, and the matte, still liquid, is charged into converters.

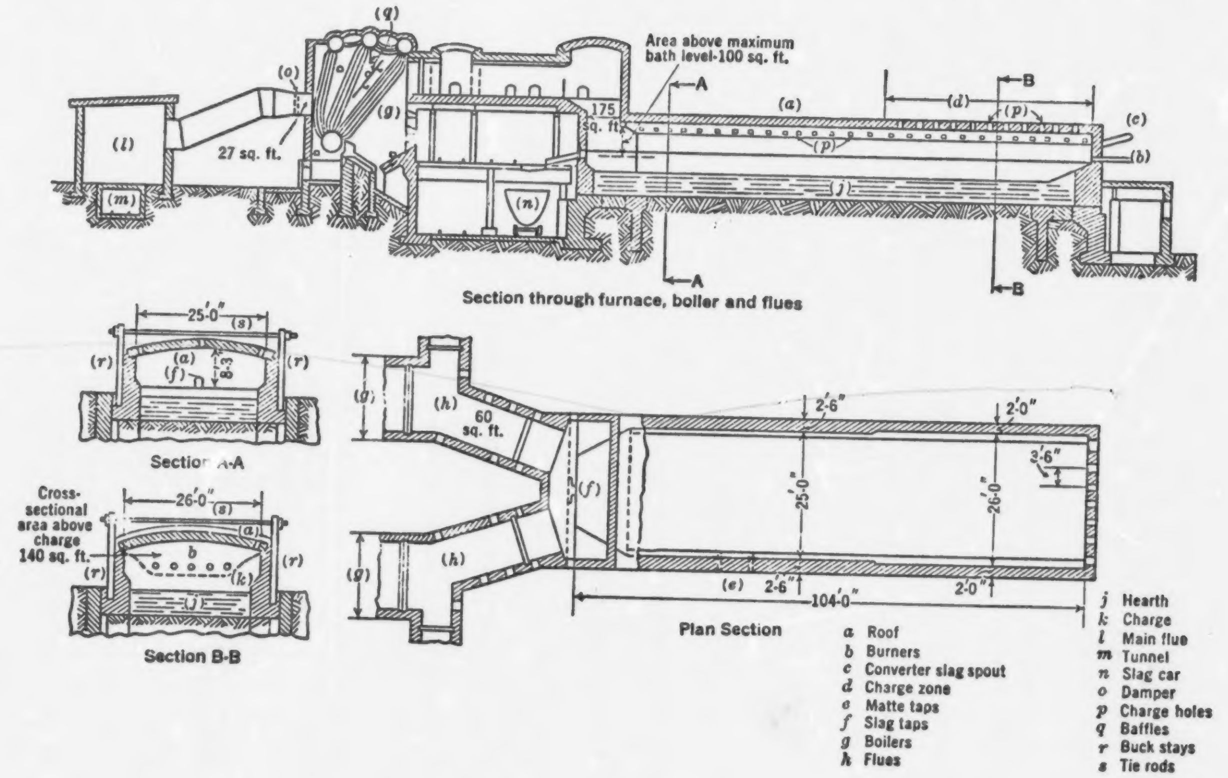

FIGURE 6. REVERBERATORY MATTING FURNACE FOR COPPER ORES(10)

Typical compositions of matte and slag are shown in the following tabulation(4):

| | Mattes | | | | Slags | | | |
|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 |
| Cu, percent | 45.0 | 43.4 | 31.6 | 27.2 | 0.6 | 0.43 | 0.40 | 0.34 |
| Fe, percent | 23.0 | 22.7 | 35.0 | 40.7 | 42.5 | 34.5 | 35.0 | 40.7 |
| S, percent | 24.0 | 25.0 | 25.0 | 24.0 | -- | -- | -- | -- |
| $SiO_2$, percent | -- | -- | -- | -- | 34.5 | 39.2 | 37.0 | 37.6 |
| CaO, percent | -- | -- | -- | -- | 5.8 | 6.8 | 5.0 | 3.5 |
| $Al_2O_3$, percent | -- | -- | -- | -- | 6.3 | 4.8 | 7.2 | 9.6 |

Converting (9)

In this step, the matte produced in the reverberatory furnace is converted to a relatively impure form of copper called blister copper by an oxidation process involving the blowing of thin streams of air through the molten material. The operation is done in two stages. In the first, the iron sulfide component of the matte is oxidized to sulfur dioxide and iron oxide, leaving nearly all of the copper as molten copper sulfide or "white metal". Sulfur dioxide leaves the converter as a gas and may be processed to sulfuric acid. Fumes and dusts which may contain lead, bismuth, arsenic, etc., produced by converting are collected and sent to lead smelters. The iron oxide which is formed during converting reacts with silica, added as a flux to the converting operation, to form a molten iron silicate slag. The reaction occurring in the first stage of converting is approximately

$$CuFeS_2 + O_2 + SiO_2 \rightarrow SO_2 + FeSiO_3 + Cu_2S \ .$$

| $CuFeS_2$ | $O_2$ | $SiO_2$ | $SO_2$ | $FeSiO_3$ | $Cu_2S$ |
|---|---|---|---|---|---|
| Matte | Added as air | Silica added for fluxing | Sulfur dioxide to sulfuric acid manufacture | Iron silicate slag removed and recirculated | Cuprous sulfide (white metal) |

When this reaction is completed, the slag is removed from the converter. Because converter slag normally contains significant concentrations of copper, it is recirculated to the matte-smelting step in the reverberatory furnace.(8) After removal of the converter slag, the blowing with air is continued until virtually all of the remaining sulfur is oxidized and removed as sulfur dioxide, in accordance with the overall equation

$$Cu_2S + O_2 \rightarrow Cu + SO_2 \ .$$

The converted copper is still relatively impure, containing varying amounts of heavy metals, arsenic, and sulfur. It also contains virtually all of the precious metals originally present in the concentrates.

This "converted" copper may be transferred while still molten to refining furnaces. Some, however, may be cast into pigs prior to subsequent refining. When cast it exhibits a typically rough upper surface upon solidification, owing to the expulsion of gases, mainly air and sulfur dioxide. This rough surface accounts for the name 'blister" copper.

Converting is done in large horizontal cylindrical furnaces up to 30 feet in length and about 12 feet in diameter, with a centrally located aperture for charging, unloading, and exit of gases. The furnaces are also fitted with numerous tuyeres along their length near the bottom through which the air necessary for converting is blown. The converters are mounted on trunnions so that they may be tilted. During the converting operation the furnaces are run in an upright position with the aperture directly beneath a hood through which the converting gases are exhausted. They are tilted or tipped for charging, discharging, and inspection.

Typical analyses of "blister" copper(10) produced by converting are shown in the following tabulation:

| Sample | Percent | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Cu | As | Sb | Pb | Ni | Zn | Fe | S | Au* | Ag* |
| 1 | 98.4 | 0.02 | 0.178 | 0.001 | 0.005 | 0.003 | 0.13 | 0.20 | 0.295 | 111.9 |
| 2 | 98.8 | 0.10 | 0.04 | 0.15 | 0.05 | 0.12 | 0.25 | 0.17 | 0.31 | 30.25 |
| 3 | 99.5 | 0.035 | 0.015 | 0.001 | 0.04 | 0.002 | 0.030 | 0.06 | 0.02 | 2.50 |

* Ounces per ton.

## Fire Refining (11)

Fire refining is a high-temperature furnacing process, involving oxidation, slagging, and reduction, by which "blister" copper is further purified to produce either a final product--"fire-refined" copper--or anodes for subsequent electrolytic refining. "Fire-refined" copper, i.e., copper which has been refined by this furnace process, constitutes only a relatively minor percentage of the total production of refined copper. Most of the primary U. S. copper is further purified by electrolytic refining.

Fire refining to produce electrodes for subsequent electrolytic refining is referred to as "anode furnace refining". The purpose of anode furnace refining is to purify and degas the blister copper so that the anodes produced will be physically and chemically acceptable for electrolysis. This refining removes the large amounts of cuprous oxide and other impurities, which, if allowed to remain in the anodes, would segregate and weaken their structure and result in rough surfaces. As is discussed under Electrolytic Refining (13), weak, nonhomogeneous anodes with nonflat surfaces complicate that operation.

Anode furnace refining is done in two kinds of furnaces:

(1) Reverberatory furnaces somewhat similar to, but considerably smaller than, the reverberatory furnaces used in matte smelting. Such furnaces are used for refining solidified blister copper that has been previously cast into pigs and remelting high-grade scrap.

(2) Cylindrical furnaces similar to but smaller than the previously described converters. These furnaces can be tilted on trunnions in somewhat the same fashion as converters and are designed to accept molten charges of blister copper directly from converters. Refining furnaces are fueled by coal, natural gas, or oil.

The operation is carried out by introducing air beneath the molten metal surface to oxidize part of the copper to cuprous oxide. The cuprous oxide, soluble in molten copper, reacts with zinc, tin, or iron present in the copper to form sulfur dioxide and metal oxides. Sulfur dioxide passes off as a gas and the oxides of iron, zinc, and tin, with added silica, form a slag that can be removed by skimming. Other impurities, such as lead, arsenic, and antimony, are only partially removed by this method. To remove large amounts of these impurities it is necessary to employ basic fluxes such as lime or soda instead of silica. Other metals that may be present in the copper, such as gold, silver, and nickel, and some of the metalloids, selenium and tellurium, resist this treatment and remain with the copper.

After oxidation and slag removal are accomplished, the copper will contain considerable oxygen as cuprous oxide which must be removed before casting anodes. Deoxidation is done traditionally by the addition of coke and by "poling". Poling amounts to inserting rather large poles of green hardwood beneath the surface of the copper and allowing them to decompose into reducing gases. These gases reduce the cuprous oxide to copper metal. An alternative for reducing the copper oxide is to pass reformed natural gas through the bath of molten copper.

After reduction, if electrolytic refining is to follow, the fire-re-refined copper is cast into anodes. If fire-refined copper is the desired end product, it is cast into various "refinery" shapes, such as wire bar, billets, cakes, and ingots.

## Fire-Refined Copper (11a)

Fire-refined copper must conform to fairly stringent requirements. The wire bar, cakes, and billets to meet specifications must contain a minimum of 99.5 to 99.85 percent copper, depending on their subsequent use. Any silver present may be counted as copper. Metal and metalloid impurities, such as arsenic, nickel, bismuth, lead, etc., are also rigidly specified.

Anodes, which represent the major tonnage of fire-refined copper, are cast into rectangular shapes of various sizes and weights, depending on specific refinery practice. A typical anode will be about 36 to 39 inches wide, 35 to 38 inches long, and about 1.25 to 1.5 inches thick, weigh from about 500 to 700 pounds, and contain about 99.5 percent of copper.

## Electrolytic Refining (13)

The purpose of electrolytic refining is to produce a very high purity copper, and, at the same time, to separate from the copper and recover the valuable metal and metalloid impurities that are present in the "fire-refined", or more properly, "anode-furnace-refined" copper.

Typical compositional ranges of anodes are shown in the following tabulation:

| | Percent |
|---|---|
| Cu | 98.5 to 99.6 |
| Pb | 0.01 to 0.32 |
| Fe | 0.01 to 0.06 |
| Bi | 0.0001 to 0.009 |
| As | 0.004 to 0.32 |
| Sb | 0.002 to 0.24 |
| Ni | 0.002 to 0.60 |
| Se | 0.01 to 0.20 |
| Te | 0.006 to 0.08 |
| Au | 0.01 to 3.5 oz/ton |
| Ag | 2.4 to 9.1 oz/ton |
| Oxygen | 0.1 to 0.3 |

Electrolytic refining is carried out in the following manner: the electrolytic tanks are rectangular vessels about 10 to 15 feet long, about 3 to 3-1/2 feet wide, and about 3-1/2 to 4 feet deep. They are usually constructed of concrete lined with lead or antimonial lead.

Each tank is fitted on the top, along each side, with heavy copper supporting bars for carrying the anodes (and cathodes) and through which the electric current flows. The anodes, cast with lugs or hooks, are hung on these bars at regulated spaces of about 3.5 to 4.5 inches apart. The cathodes are thin sheets of electrolytically refined copper 1 to 2 inches longer and wider than the anodes, but only about 0.025-inch thick and weighing approximately 8 to 10 pounds. These cathodes, called "starting" sheets, are made in a separate section of the refinery. The starting sheets are fitted with loops of copper at their tops, through which copper bars are inserted. The copper bars serve the same function as the lugs on the cathode. When loaded, the electrolytic tank will contain from 30 to 40 cathodes and anodes, depending on the length of the cell and the spacing.

These anodes and cathodes are immersed for virtually all of their height in the electrolyte, a dilute solution of sulfuric acid and copper sulfate. Typical electrolytes contain about 40 grams per liter of copper and up to about 200 grams per liter of free sulfuric acid. When loaded, the cell is returned to operation in the refining circuit. The entire refining circuit may consist of hundreds of such tanks, arranged in optimum configurations for the circulation of the electrolyte from tank to tank, the electrical current flow, and the systematic operation of the refinery.

When electricity is flowing, the current first traverses the anodes, where copper and impurities such as nickel, arsenic, and iron are electrolytically oxidized and put into solution. Gold, silver, selenium, and tellurium do not oxidize and go into solution, but enter the electrolyte as finely divided solids called slimes which may settle to the bottom of the tank.

The current then traverses the electrolyte to the cathode where reduction or deposition of the copper takes place. This is a highly selective operation wherein soluble impurities such as nickel, arsenic, bismuth, and antimony are not deposited with the copper so long as they are kept below certain concentrations in solution. Operating conditions and schedules for preventing or minimizing the effect of such interferers have been thoroughly developed.

As the copper is deposited, the current traverses the cathode and enters a so-called support bar which connects to the next tank in line and which becomes the anode bar for that tank. Here, the same process is repeated and rerepeated through the entire circuit.

After operation for about 2 weeks, by which time the cathode of pure copper has grown to a weight of about 40 percent of that of the original anode, the cathode is removed and washed and new starting sheets are inserted on each side of the anode. The electrolysis is resumed for another period of about 2 weeks to produce a second cathode of approximately the same weight. The anode, now 80 to 90 percent consumed, is removed from the tank, and sent back to the anode refining section of the plant where it is remelted to be recast into full-sized anodes. Complete or nearly complete dissolution of anodes in the electrolytic process is impractical, and would lead to mechanical failures of the metal, with attendant short circuiting.

Periodically, the slimes which have accumulated in the tanks and which contain precious metals and other values are removed and are sent to refining operations for the recovery of these values.

During electrolytic refining, there is a continuing buildup of soluble impurities such as nickel, arsenic, antimony, and bismuth in solution. Control of the concentration of these impurities to tolerable limits is achieved by either continuously or intermittently withdrawing a portion of the electrolyte from the circuit and replacing it with fresh solution.

Various methods are employed for the recovery of copper and other values in this withdrawn or "bleed-off" solution. In the most widely practiced method, the copper in the bleed-off solution is electrolytically stripped by passing the solution through cells, similar to the refining cells but employing insoluble (e.g., iron) anodes in place of copper anodes. In this operation, where there is no copper anode to continuously supply copper to the solution, the effect of the electrolysis is to drive the copper out of solution as copper metal onto a cathode. This stripping, considerably less electrically efficient than the refining electrolysis, may be done in stages, with the first stage recovering most of the copper as a refined grade, the second as an intermediate grade suitable for casting or alloying, and the final as a low-grade copper-arsenic sludge which requires subsequent treatment. After such stripping, the soluble impurities remaining are crystallized by evaporation, the salts (such as nickel sulfate) recovered, and the acid returned to the refining circuit.

### By-Product Slimes (13a)

An important by-product of electrolytic refining is the slimes, or anode mud, which accumulate in the system and which may amount to as much as 1 to 15 percent by weight of the original anode. This mud contains virtually all of the lead, selenium, tellurium, gold, and silver originally present in the anode, a major portion of the bismuth and antimony, and a lesser proportion of the arsenic.

Typical ranges of anode mud analyses are shown in the following tabulation:(11)

| | Percent | Oz/Ton | Remarks |
|---|---|---|---|
| Copper | 10-55 | -- | Can be largely removed by screening (to about 1 to 2%) |
| Gold | -- | 0.1-500 | -- |
| Silver | -- | 25-10,000 | -- |
| Lead | <.1-15 | -- | -- |
| Antimony | <.1-16 | -- | -- |
| Sulfur | <.1-2 | -- | -- |
| Selenium | <.1-8 | -- | -- |
| Tellurium | 1-12 | -- | -- |
| Iron | 0.1-0.2 | -- | -- |
| Arsenic | 0.1-7.3 | -- | -- |
| Nickel | 0.1-0.9 | -- | -- |

## Cathode Copper (14)

The following tabulation shows the compositional range of electrolytic cathodes:

| Element | Percent |
|---|---|
| Copper | 99.95 |
| Arsenic | 0.0001 to 0.001 |
| Antimony | 0.002 to 0.001 |
| Bismuth | 0.00001 to 0.0002 |
| Lead | 0.0002 to 0.001 |
| Nickel | 0.0001 to 0.002 |
| Selenium | 0.0003 to 0.001 |
| Tellurium | 0.0001 to 0.0009 |
| Gold | 0.002 to 0.01 oz/ton |
| Silver | 0.05 to 0.5 oz/ton |

In addition, hydrogen, resulting from the electrolysis, may be present in small amount.

Some electrolytic cathodes may be sold as such, but by far the bulk of the cathodes produced are melted, given a form of fire refining, and cast into various refinery shapes.

## Melting and Casting (15)

This operation is generally referred to as cathode refining and casting. Strictly speaking, it is not refining because, in many cases, the resultant product contains slightly less copper than the cathodes themselves. Its main purpose is to produce the conventional cast refinery shapes of refined copper. In melting the cathodes to accomplish this, sulfur and oxygen are introduced from air, coke, etc., with which the copper comes in contact. Preparatory to casting, these must be removed and the oxygen controlled to produce forms that are physically and chemically acceptable by established commercial standards.

The operation is carried out in either reverberatory furnaces of the type used in fire refining (11) or in electric furnaces. When electric furnaces are used, the refining operations to remove sulfur and control oxygen are not required.

## Refinery Shapes (16)

Electrolytic copper after melting is cast into wire bar, billets, and cakes as is fire-refined copper, to meet established commercial standards for physical, chemical, and electrical properties.

## Leaching-Grade Ores (17) (Route II, Figure 4)

The major tonnage of leaching-grade ores fall into two categories:

(1) Ores containing sulfide minerals which are so fractured or shattered in texture that air and water can be made to percolate through them as they exist in the ground. Ore bodies of this type occur at several places in Arizona and Tennessee. As will be discussed later, such ores may be profitably leached "in place" without being mined.

(2) Ores containing either sulfides or mixtures of sulfides and oxide minerals which are too low in grade to justify the cost of milling. Such ores are generally encountered in large quantities in open-pit mining in the process of uncovering concentrating-grade ores. These ores, which must be removed in any event to permit systematic mining of concentrating-grade ores, are generally treated by heap leaching.

Other types of leaching-grade ores exist which are most profitably treated by specialized methods. These are discussed in later sections of this report.

## Heap Leaching and Leaching in Place (18)

Heap leaching consists in piling or dumping low-grade sulfide or mixed sulfide ore rocks in large piles, in natural basins or specially prepared areas with good drainage characteristics, and circulating dilute acidic solutions through them. In the most improved form of heap leaching, the site of the heap is carefully prepared to insure that the leach solution, after it has traversed the pile, will not be lost by permeating into the ground, but will all be contained in the system for subsequent copper recovery. In most cases, the ore as mined, which may range from boulder size to a few inches, constitutes the feed to the heap. In some cases, preliminary crushing or secondary blasting may be used to reduce large boulders so as to permit better contact of the copper minerals with the leach solution. When a heap or "dump" is prepared, a leach solution, essentially dilute sulfuric acid, is distributed evenly over the top of the pile and allowed to trickle through the pile. Such heaps may occupy scores of hundreds of acres and be scores of feet in depth. After traversing the pile, the leach solution drains to prepared reservoirs at the base of the pile, from where it is recirculated by pumping back to the distributing system on top of the pile and to subsequent copper-recovery operations.

In heap leaching, the oxide copper minerals dissolve directly in the leach solution according to the equation

$$CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O.$$

The dissolution of sulfide minerals, however, is slower and indirect, and requires oxidation.

$$CuS + SO_2 \rightarrow CuSO_4.$$

One method of achieving such oxidation is to sectionalize the heap and allow selected sections to drain completely and to aspirate air, while other sections are still being leached. After a period during which the air has oxidized the copper sulfides to copper sulfate, leaching in the section is resumed, with the consequent dissolution of copper sulfate.

The presence of ferric sulfate in the leach solution also promotes the oxidation of copper sulfides, by a reaction similar to

$$4Fe_2(SO_4)_3 + CuS + 4H_2O \rightarrow 8FeSO_4 + CuSO_4 + 4H_2SO_4.$$

In recent years, patents have been issued covering the employment of bacteria as leaching aides. These bacteria are said to produce both ferric sulfate and sulfuric acid, which are the effective leaching media.

Pregnant solutions from the heap-leaching operations, containing up to several grams per liter of copper as copper sulfate, are then treated by various copper-recovery processes such as cementation or solvent extraction. These are discussed later.

Leaching in place is generally done on depleted ore bodies or on ore bodies too low in grade to justify conventional mining. An essential to leaching-in-place methods is a well-fractured deposit, which will permit the permeation of leach solution and air. Leaching in place is done by the intermittent circulation of leach solution and air through such deposits, the air being required for oxidation of sulfide minerals. The pregnant solution from in-place leaching drains into tunnels cut beneath the deposit and is pumped to the surface for copper-recovery treatment, generally by cementation.

Percolation leaching and agitation leaching, applicable mainly to large deposits of oxide ores, are discussed later in the report.

## Copper Solutions From Leaching (19)

The pregnant solutions derived from leaching normally contain up to several grams per liter of copper as copper sulfate. The method does not recover gold, silver, selenium, and tellurium that are valuable by-products of the smelting operation. Solutions from this type of leaching are too dilute for the recovery of copper by direct means, such as electrolysis, and must be treated by an intermediate concentration process such as cementation or solvent extraction.

## Cementation (20)

Cementation is a process whereby copper in solution is precipitated or "cemented" out of solution as a finely divided metallic product by replacement with some less noble (that is, more active) metal. In the copper industry, scrap iron is the cementing metal used. The scrap iron may be in the form of salvaged tin cans, factory scrap such as punch plate, or drillings, automobile scrap, baling wire, etc. Massive scrap, such as rails, may be used at the head end of a penetration launder to reduce any ferric sulfate in solution. Tin cans are preferred.

Cementation is carried out by directing the flow of copper solution through launders (or channels) loaded with scrap iron. As the solution flows through the bed of iron, the reaction

$$\underset{\text{solution}}{Fe + CuSO_4} \rightarrow \underset{\text{precipitated}}{Cu} + \underset{\text{solution}}{FeSO_4}$$

occurs, the copper depositing in loosely adherent form on the iron surfaces from which it may be easily detached by washing. Cementation operations are so designed and scheduled that when a launder or section of launder is loaded with copper, it may be taken out of the circuit and the copper washed out of the system through screens into settling basins by means of high-pressure water sprays. Washing techniques vary. In some cases, they are highly mechanized, employing machines called "sweepers" which traverse the length of the launder directing high-velocity jets of water into the scrap and driving the fine cement copper into settling basins. In others, high-pressure, manually operated hoses are employed. Powerful electromagnets are used to remove iron from the launders to expose cement copper to the action of the wash waters.

In the cementation process, iron, which replaces copper in solution, is consumed. The theoretical consumption is about 0.9 pound of iron per pound of copper. In actual practice, iron consumption is generally much higher, owing to side reactions with free acid and ferric sulfate in the leach solutions

$$H_2SO_4 + Fe \rightarrow FeSO_4 + H_2$$

$$Fe_2(SO_4)_3 + Fe \rightarrow 3FeSO_4.$$

Cementation recovers virtually all of the copper from the leach solution, leaving a barren or stripped solution containing ferrous sulfate and some free acid. Such solutions are returned to leaching operations with or without the addition of more sulfuric acid.

## Cement Copper (21)

The product of cementation is called cement copper. It is a relatively impure material containing from about 70 to 90 percent copper and contaminated with such materials as shards of scrap iron which escaped screening; dirt, waste, rust, etc., introduced with the scrap iron; basic copper and iron sulfates originating from occlusion or adsorption of sulfates from the leach solution; and considerable oxygen, the result of the atmospheric oxidation of the highly reactive fine copper particles. Most cement copper produced in the United States is sent to smelters where it generally is fed to the reverberatory matte furnaces. In a few cases, it may be beneficiated by physical and/or chemical processes to an acceptable grade of copper powder for use in powder-metallurgy applications.

## Solvent Extraction (22)

Solvent extraction is a new technique for recovering copper from leach solutions, adopted recently by several western companies to supplant cementation. In this process, the dilute leach solutions are contacted with relatively small volumes of an organic solvent which selectively extracts copper into the organic phase.

The organic solution containing the copper is then contacted with a relatively small volume of aqueous "stripping" solution under conditions of acidity that cause the copper to leave the organic phase and enter the aqueous stripping phase. The resulting solution, containing upwards of 30 grams per liter of copper, is now sufficiently concentrated and pure for subsequent treatment by electrolysis to produce cathode copper.

## Electrowinning (23)

Electrowinning is the term given the process of electrolyzing or depositing copper from leach solutions in the form of cathodes, of a purity comparable to electrolytically refined copper. The overall principles, operation, and results associated with electrowinning are similar to those of electrolytic refining (16) with these exceptions:

(1) Copper anodes which supply the feed of copper to electrolytic refining cells are not used in electrowinning. Insoluble anodes (mainly antimonial lead) are substituted and the copper feed to electrowinning

cells is in the form of solution, either from the solvent extraction process (25) or from specialized leaching operations (34-35) which are discussed later (see Figure 4). Cell construction, electrical hookups, starting sheets, etc., are similar to those used in electrolytic refining.

(2) Power requirements for electrowinning are 8 to 10 times greater than for electrolytic refining, but this factor is offset to some extent by lower labor costs.

(3) Because long-life, insoluble anodes are used in electrowinning, some of the major cost items of electrorefining are minimized. Cathodes produced by electrowinning operations are melted and cast into the conventional refinery shapes.

### High-Grade Sulfide Ores (24) (Route III, Figure 4)

High-grade ores are almost exclusively the product of underground mining. They may range in grade from about 3 to 10 percent of copper. They constitute a minor portion of the copper production. As shown in Figure 4, they may be smelted directly or sent to concentrators, depending on economic considerations.

### Mixed Sulfide-Oxide Ores (25) (Route IV, Figure 5)

These are the ores which are concentration grade (about 0.8 to 1.0 percent copper), but in which the copper values occur as both sulfide and oxide minerals. Sulfide minerals are, as has been explained earlier, amenable to concentration. Oxide minerals are only partially so. It has been stated that the loss of oxide minerals in flotation may amount to as much as 50 percent. Special recovery methods are therefore applied to these mixed ores.

Two such processes are

(1) Preliminary percolation or "vat" leaching to recover oxide copper, followed by treatment of the leach residue in concentrators to recover the sulfide minerals

(2) The so-called leach-precipitation-flotation procedure.

### Vat Leaching--Concentration (30)

In this process the ore--a mixture of sulfide and oxide minerals--is crushed to about 3/8 inch in size and first leached by the percolation or "vat leaching" technique described in detail later in the report. This extracts upwards of 90 to 95 percent of the oxide copper present and recovers it in concentrated solutions which can be electrolyzed to produce cathode copper (23) and/or dilute solutions which must be treated by some concentration process such as cementation (20).

After removal of the oxide copper, the residue, containing practically all of the sulfide copper originally present, is excavated from the vats and transferred to a concentrator where the sulfide copper is recovered by flotation (4).

## Leach-Precipitation-Flotation (27)

This is an alternative process for treating mixed sulfide--oxide ores. In this process, the ore is leached in dilute sulfuric acid to solubilize oxide copper minerals. The ore is first crushed and ground and separated into sand (relatively coarse granules) and slime (fine powder) fractions. The sands, which account for about 80 percent of the weight of the original ore, are leached in dilute sulfuric acid to dissolve the oxide copper from the oxide minerals. After washing, they are further ground and treated by conventional flotation processes to recover copper sulfides in the form of flotation concentrates. The pregnant solution from the leaching of the sands is then used to leach copper from the slimes in agitated tanks. After this secondary leaching, sponge iron (i.e., fine powder) is added to the mixture of copper solution and slimes. This precipitates the dissolved copper as metallic "cement" copper. This "cement" copper, which responds to flotation much as do copper sulfide minerals, is recovered by a modified procedure as a flotation concentrate which is combined with the flotation concentrate from the treatment of the sands.

## Native Copper Ores (28) (Route V, Figure 4)

Native copper ores occur predominantly in Michigan in the Lake Superior District. In the mines now being worked in that state, native copper constitutes only a small percentage of the value, with chalcocite being the major copper mineral. In times past, when native copper was an important constituent of the Michigan ores, specialized concentration procedures were employed to recover it. These included stamp-milling, jigging, tabling, etc. At the present time, the Michigan ores, all underground, are treated by more or less conventional concentration and refining methods.

## Oxide Copper Ores (29) (Route VI, Figure 4)

Some ores, notably in Arizona and Nevada, are predominantly oxide ores containing chrysocolla, azurite, and malachite. If sufficiently high grade, which is a rare occurrence, they may be sent directly to smelters. If low grade (less than about 1.5 to 2 percent), these oxide ores are treated by various leaching techniques. Very low-grade oxide ores were discussed earlier and may be heap leached (18). Those containing upwards of about 0.8 percent copper are generally leached by percolation or vat-leaching processes.

## Vat Leaching (30)

In vat or percolation leaching processes, the ore is first crushed to about 3/8 to 1/2 inch in size and loaded into vats. These vats are walled concrete structures of various sizes, ranging in capacity from a few hundred tons up to 20,000 tons of ore. The floors of leaching vats are, in effect, filters which will permit the upflow or downflow of leach solutions and wash solutions. Vat floors are constructed in various ways as with timbers, graded gravels, sand, fiber matting, etc. The vats are usually arranged in banks or groups, with a common wall between adjacent vats. The number of vats in a bank may range from 6 to more than 12. Auxiliary piping, drains, sumps, pumps, tanks, etc., are arranged to accommodate the required flow pattern of leaching and washing solutions through the system. Conveyor-belt systems provide the most efficient and satisfactory methods for loading ore into vats, although smaller installations may employ such means as front-end loaders, drag scrapers, etc. Unloading or excavating after leaching, in the larger plants, is done by traveling clam shells.

Leaching in vats is a carefully designed and executed process aimed at extracting upwards of 90 percent of the copper in the ore. It is accomplished by passing dilute sulfuric (about 2 to 5 percent) acid solution through the crushed ore mass in the vats by upflow percolation, downflow percolation under flooding conditions, or downflow nonflooded percolation (i.e., by spraying or otherwise distributing leach solution onto the top surface of the ore and permitting it to trickle down through the ore).

The pattern of leaching varies from installation to installation, depending on the reactivity of the copper minerals in the ore, the number of vats provided, acid strength, components of the gangue, solution concentrations desired, etc. Commonly, the countercurrent pattern is followed in which leach solution from one vat is advanced to the next containing a new charge.

Complete dissolution of the recoverable copper to sulfate may require a week or more. After conversion of the copper oxides to soluble copper sulfate is accomplished, it is necessary to wash the ore free of soluble copper. This is done by a countercurrent process in which fresh wash water is added to the vat next to be discharged and passed then to the adjacent vat. Storage tanks for wash waters representative of various washing stages are provided in the larger installations.

Pregnant solutions of various strengths may be prepared, depending on the leaching pattern. In some installations the pregnant solution may comprise both the leach and wash solutions. In some of the larger plants, leach solutions containing up to 35 grams per liter of copper are withdrawn and sent to electrowinning processes. The wash solutions generated in these cases will be considerably diluted, and are treated by cementation or solvent extraction.

### By-Product Copper Ores (31) (Route VII, Figure 4)

Much of the by-product copper comes from lead-zinc, molybdenum, or iron ores. Most of it is received and separated from the circuit by selective flotation processes developed for the treatment of these ores. In one case, where copper is the by-product of iron-ore beneficiation, the copper is recovered by a combination of leaching and cementation.

# SECTION VI

## THE SELENIUM AND TELLURIUM INDUSTRY

### Size and Characteristics

There are no selenium and tellurium ores; hence there is no selenium or tellurium mining or concentration. The principal, if not the only, raw material for the recovery and refining of these metalloids in the United States is the electrolytic slimes, a by-product of copper refining. A minor contributor to selenium-tellurium production may be the fumes and dusts from lead-smelting operations.

In terms of mass, the industry is small. In 1969, for example, total selenium production in the United States was about 600 tons, while tellurium production was about 120 tons. This production was distributed among the seven companies shown in Table 6.(1)

TABLE 6. UNITED STATES PRODUCERS OF SELENIUM AND TELLURIUM METALS AND COMPOUNDS

| | Se | Te |
|---|---|---|
| American Metal Climax, Carteret, N.J. | X | X |
| American Smelting and Refining Co., Baltimore, Md. | X | X |
| International Smelting and Refining Co., Perth Amboy, N.J. | X | X |
| Kennecott Copper Corp., Garfield, Utah | X | |
| Kawecki-Berylco Industries Inc., Boyertown, Pa. | X | |
| Phelps Dodge Refining Corp., Maspeth, N.Y. | X | X |
| U.S. Smelting Lead Refinery, Inc., East Chicago, Ill. | | X |

### Raw Materials and Processes

Anode slimes, as discussed previously in the section of this report dealing with copper, are complex mixtures of base metals, precious metals, and selenium and tellurium. The precious metals, silver and gold, are by far the major values in slimes. Consequently, the

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processes which are used to recover and refine selenium and tellurium are designed also to recover precious metals.

Several processes, all of them intricate and requiring considerable care and personal attention by operators, are available.(22,23)

Figure 7 is a flow diagram showing one of the approaches. As shown in this figure, the slimes--previously decopperized by leaching with sulfuric acid (as described under copper)--are smelted in a small reverberatory furnace, called a Doré furnace. The first slag which forms is removed; sodium carbonate and sodium nitrate in the weight ratio of 2:1 is then added. The soda slag formed contains selenium and tellurium. During smelting, some selenium and tellurium are lost from the Doré furnace by volatilization. These are recovered by scrubbing the fumes with water.

The soda slag is ground in a rod mill and leached in hot water to dissolve selenium and tellurium; the slurry is filtered and the filtrate containing most of the selenium and tellurium is combined with the scrubber water which contains the selenium and tellurium lost from the Doré furnace. Although not shown in Figure 7, gold and silver are recovered as Doré alloy from the Doré furnace.

The combined filtrate and scrubber water are neutralized with sulfuric acid to a pH of about 5.5. At this pH, tellurium precipitates and is filtered off and sent to a series of refining steps. The solution containing selenium is acidified with sulfuric acid and treated with sulfur dioxide gas. This treatment precipitates selenium as metal which is filtered, dried, and packaged for shipment. The finished selenium product has a minimum purity of 99.5 percent.

The filter cake containing tellurium is treated with sodium hydroxide-sodium sulfide solution to redissolve tellurium. Precious metals that may be present at this stage remain in the insoluble residue, are separated by filtration, and are returned to the Doré furnace. The solution containing tellurium as sodium tellurite is neutralized with sulfuric acid to a pH of 5.5 whereupon tellurium reprecipitates as purified tellurium dioxide ($TeO_2$). This may be dried, ground, and sold as such, or reduced to metal by carbon in a crucible and cast into ingots.

Numerous variations of this process are practiced by other companies. This process and the variations of it are the result of much research and process development work undertaken by the companies to determine optimum conditions for treating their particular feed materials.

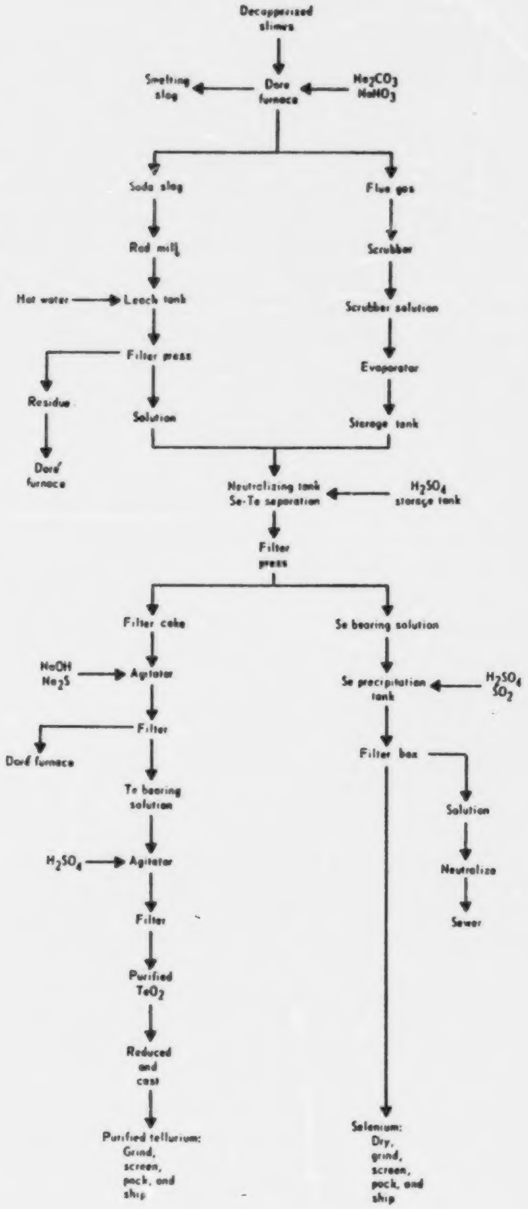

FIGURE 7. FLOWSHEET OF SELENIUM-TELLURIUM RECOVERY PROCESS(23)

(Courtesy, United States Metals Refining Co., Division of American Metal Climax, Inc.)

# SECTION VII

## WATER USAGE IN THE COPPER INDUSTRY

Data on water usage were obtained for about 30 copper-producing facilities in the country. Some of the data were gathered from the open literature, but the major and most meaningful data were obtained from information supplied by copper-producing companies.

Table 7 is a general picture of the coverage achieved in the study. The table shows the gross intake and discharge volumes reported by respondents for the indicated copper-producing facilities. The first line of the table, for example, shows that a copper mining and leaching operation used 1,066 million gallons per year of water and discharged 45.4 million gallons per year of this as waste. The data also indicate that a number of mining and milling operations (Lines 3-10, e.g.) which use large quantities of water produce no waste effluent at all. Such facilities, located in water-scarce sections of the country, recirculate as much water as possible to their processing. Water consumption in these instances is due to evaporation and seepage into the ground.

Table 8 is an extension of these data to show total water use (including recirculated water) and the intake, use, and consumption of water per ton of metal produced for various associations of facilities (mining and leaching, mining and concentrating, etc.).

The values shown in Table 8 indicate the wide variation in water-utilization practices. The category of "mine and concentrator" operations should represent the simplest case, with minimal variations in process technology or operations. Yet even here, the water use in gallons per ton of contained metal, a term which should approach expression of the common features of the process, varies by more than a factor of ten, i.e., from 13,000 to over 190,000 gallons per ton of contained metal. The explanation for this variation would require a specific study of the operational details not disclosed in this investigation.

Copper mining and leaching operations, represented by three examples in the table, show about the same tenfold variation in water usage per ton of metal (15,000 vs 147,000). Two of these show the high recycle practice that is characteristic of the industry as a whole. The operation showing the lowest of the three recirculation rates (773 MGY) may need to decrease, in the future, losses to seepage, but additional data would be required to confirm this.

In the category of "Mine, Concentrator, and Smelter", the water usage and consumption per ton of metal and the recirculation rate fall into a reasonably closely grouped pattern. Specific studies based on additional information would be necessary to explain the variations in water

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## TABLE 7. SAMPLE OF COPPER-PRODUCING OPERATIONS

| | Operations | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Mine | Mill | Leach | Smelter | Refinery | Power Plant | Acid Plant | Other | Intake, MGY(a) | Discharge, MGY(a) |
| 1 | X | -- | X | -- | -- | -- | -- | -- | 1,066 | 45.4 |
| 2 | -- | -- | X | -- | -- | -- | -- | -- | 630 | 120 |
| 3 | X | -- | X | -- | -- | -- | -- | -- | 4,760 | 0 |
| 4 | X | X | X | -- | -- | -- | -- | -- | 2,170 | 0 |
| 5 | X | X | -- | -- | -- | -- | -- | -- | 2,560 | 0 |
| 6 | X | X | -- | -- | -- | -- | -- | -- | 1,980 | 0 |
| 7 | X | X | -- | -- | -- | -- | -- | -- | 949 | 0 |
| 8 | X | X | -- | -- | -- | -- | -- | -- | 795 | 0 |
| 9 | X | X | X | -- | -- | -- | -- | -- | 363 | 0 |
| 10 | X | X | X | X | -- | -- | X | -- | 3,960 | 0 |
| 11 | X | X | -- | X | -- | X | -- | -- | 2,310 | 5.14 |
| 12 | X | X | -- | X | -- | -- | -- | -- | 437 | 0 |
| 13 | X | X | -- | X | | | | | 4,204 | 0 |
| 14 | -- | X | -- | X | -- | X | X | -- | 4,230 | 2,780 |
| 15 | -- | X | -- | X | -- | X | -- | -- | 6,810 | 625 |
| 16 | X | X | -- | X | X | -- | -- | -- | 3,510 | 0 |
| 17 | -- | -- | -- | X | -- | X | -- | -- | 610 | 0 |
| 18 | -- | -- | -- | X | -- | -- | -- | -- | 540 | 0 |
| 19 | -- | -- | -- | X | -- | -- | X | -- | 5,820 | 1,130 |
| 20 | -- | -- | -- | X | X | -- | -- | -- | 1,930 | 1,720 |
| 21 | -- | -- | -- | X | X | -- | X | -- | 6,875 | 6,600 |
| 22 | -- | -- | -- | -- | X | -- | -- | -- | 456 | 2.4 |
| 23 | -- | -- | -- | -- | X | -- | -- | -- | 656 | 605 |
| 24 | -- | -- | -- | -- | X | -- | -- | -- | 804 | 733 |
| 25 | -- | -- | -- | -- | X | -- | -- | -- | 210 | 75.2 |
| 26 | -- | -- | -- | -- | X | -- | -- | -- | 297 | 120 |
| -- | XX | X | X | X | X | X | -- | -- | 39,350 | 29,720 |
| | 14 | 15 | 6 | 13 | 9 | 5 | 4 | | 98,282 | 44,280 |

(a) Million gallons per year.

## TABLE 8. WATER DATA FOR COPPER-PRODUCING FACILITIES

| Total Water Intake, MGY(a) | Discharge to Receiving Waters, MGY(a) | Total Use New and Recirculated, MGY(a) | Gallons Intake per Ton of Metal | Gallons Used per Ton of Metal | Consumption (Intake Minus Discharge), gallons per ton of metal |
|---|---|---|---|---|---|
| | | **Mine and Concentrator** | | | |
| 2,170 | 0 | 6,410 | 28,900 | 85,400 | 28,900 |
| 2,560 | 0 | 3,720 | 43,700 | 63,200 | 43,700 |
| 1,980 | 0 | 9,300 | 41,200 | 193,000 | 41,200 |
| 949 | 0 | 2,740 | 36,000 | 104,000 | 36,000 |
| 795 | 0 | 2,770 | 26,500 | 92,300 | 26,400 |
| 363 | 0 | 480 | 9,070 | 13,300 | 9,100 |
| | | **Mine and Leaching Operations** | | | |
| 1,070 | 45.4 | 7,670 | 20,500 | 147,000 | 19,600 |
| 630 | 120 | 773 | 12,600 | 15,500 | 10,200 |
| 4,760 | 0 | 25,000 | 16,300 | 85,500 | 16,300 |
| | | **Mine, Concentrator, and Smelter** | | | |
| 3,960 | 0 | 16,300 | 30,400 | 125,000 | 30,400 |
| 2,310 | 5.1 | -- | 32,600 | -- | 31,100 |
| 437 | 0 | | 21,900 | | |
| 4,200 | 0 | 17,500 | 41,000 | 175,000 | 41,000 |
| 3,510 | 0 | 31,500 | 28,400 | 254,000 | 28,400 |
| | | **Concentrator and Power Plant** | | | |
| 32,600 | 19,500-28,500 | 144,000 | 130,000 | 573,000 | 16,500-52,300 |
| | | **Concentrator and Smelter** | | | |
| 4,230 | 2,780 | 6,850 | 56,100 | 91,000 | 19,300 |
| 6,740 | 625 | 7,830 | 136,000 | 156,000 | 124,000 |
| | | **Smelter** | | | |
| 610 | 473(b) | 980 | 6,400 | 10,300 | 1,100 |
| 540 | 0 | 5,280 | 3,650 | 39,300 | 3,650 |
| 5,820 | 1,130 | 19,900 | 17,900 | 61,400 | 16,100 |
| | | **Refinery** | | | |
| 456 | 2.4 | 3,730 | 1,070 | 8,770 | 1,070 |
| 656 | 606 | -- | 2,390 | -- | 182 |
| 804 | 734 | 3,320 | 3,470 | 14,300 | 304 |
| 210 | 75.2 | 256 | 763 | 927 | 490 |
| 297 | 297 | 297 | 1,600 | 1,600 | 0 |
| | | **Smelter and Refinery** | | | |
| 1,930 | 1,720 | 9,110 | 9,670 | 45,500 | 1,100 |
| 6,875 | 6,600 | 8,510 | 42,800 | 52,900 | 1,710 |

(a) Million gallons per year.

(b) Receiving "water" is a watercourse which is normally dry; it carries "natural" runoff during seasonal rains.

usage consumption and recirculation calculated for the groupings "Concentrator and Smelter", "Smelter", and "Smelter and Refinery". These variations are probably associated with such factors as size, location, technical and economic considerations, etc.

The data in Table 9, also derived from information supplied by producers, shows the allocation of new water by percentage to various phases of the operation (process, cooling, boiler feed, air-pollution control, sanitary, and miscellaneous) for various associations of facilities. The table also shows the degree of recycling practiced in the entries under "Use Ratio".

## Waste-Water Sources, Characteristics, and Amounts

The ways in which water is used and waste is generated in the copper industry in metallurgical operations are indicated in Figures 8 through 10. These figures are generalized flowsheets based on information supplied to this survey. Water sources for mines and concentrators include wells, surface waters, or mine water itself. The waters may be treated in any number of ways before use, but the most common are indicated: potable (sanitary) water is usually chlorinated and, if necessary, clarified by flocculation, filtering, etc. It may also be softened, depending on the quality of the source. The potable water may be obtained from a nearby municipal supply. The sanitary water circuit includes drinking water, change-room showers, toilets, etc. In the case of isolated operations, the circuit includes the nearby townsite in its entirety. All plants either treat the sanitary wastes or discharge to a municipal sewer (which may, as indicated above, be corporate operated). Plant sewage-treatment effluents may go to ground in isolated, desert operations, to surface or estuarine receivers, or be recirculated to the metallurgical process. Another common use of water in mining operations (as shown in Figure 8) is for dust control, in areas of underground or open-pit mining, ore-haulage roads, drill "cooling", or at dusty process areas (primary crushers, conveyor transfer points, etc.). Most of such water remains in the ore as moisture and follows a recirculation path with the ore to the concentrator. The remainder of such water is lost to ground or to evaporation.

Flotation requires large amounts of water, which is recirculated to the process after dewatering tailings and concentrates in thickeners, classifiers, filters, etc. The thickening operation produces an overflow of substantially clear water, which is immediately recirculated. The underflow of the thickener is tailings slurry which is pumped to a tailing disposal site. Here the solids settle slowly and the clear water is either discharged or recycled.

Most mining and milling operations require steam generators, with the steam being used for electrical-power generation or general plant use. Cooling water may be recirculated through a cooling tower or spray

TABLE 9. WATER USES AND RECIRCULATION PRACTICE IN COPPER PRODUCING MINES AND PLANTS

| Percent of New Water | | | | | | Use Ratio[a] by Process | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Process | Cooling | Boiler Feed | Air Pollution Control | Sanitary | Other | Process | Cooling | Boiler Feed | Air-Pollution Control | Sanitary | Other | Overall |
| | | | | | Mine and Leaching Operation | | | | | | | |
| 28.3 | 7.4 | 4.3 | 51.3 | 8.7 | - | 2.0 | 1 | 1 | 1 | 1 | (b) | 7.3 |
| 91.1 | 2.1 | 0.5 | 3.0 | 3.2 | -- | 1.7 | 1 | 1 | 1 | 1 | -- | 1.6 |
| 86.3 | -- | -- | 6.5 | 7.2 | -- | 6.5 | -- | -- | 1 | 1 | -- | 5.7 |
| | | | | | Mine and Concentrator | | | | | | | |
| 82.2 | 1.2 | 0.4 | 11.4 | 1.4 | 3.5 | 3.1 | 21.2 | 1 | 1 | 1 | -- | 3.0 |
| 96.2 | -- | -- | 0.3 | 3.5 | -- | 1.6 | 1 | -- | 1 | 1 | -- | 1.6 |
| 97.8 | -- | -- | 1.9 | 0.3 | -- | -- 5.2 | --(c) | -- | 1.01 | | -- | 5.2 |
| 84.6 | -- | -- | 7.7 | 7.7 | -- | 3.1 | -- | -- | 2.0 | 1 | -- | 2.9 |
| 68.2 | -- | -- | 9.1 | -- | 22.7 | 4.4 | -- | -- | 2.0 | -- | 1.21 | 3.5 |
| 86.2 | 5.5 | 3.7 | >0.1 | 4.6 | -- | 1.8 | 1 | 1 | -- | 1 | -- | 1.7 |
| | | | | | Mine, Concentrator, and Smelter | | | | | | | |
| 71.4 | 8.7 | 0.2 | 3.2 | 16.5 | -- | 4.3 | 1 | 1 | 7.75 | | | 4.11 |
| 86.8 | 2.9 | 7.1 | 2.9 | 0.3 | -- | -- | -- | -- | -- | -- | -- | -- |
| 64.3 | 12.8 | 13.8 | 4.0 | See Boiler Feed | 5.1 | 4.0 | 3.2 | | | | | 4.0 |
| 90.2 | 5.5 | 1.5 | 2.7 | 0.1 | -- | 2.4 | 123.8 | 7.6 | 2.0 | 2.0 | -- | 9.2 |
| | | | | | Concentrator and Power Plant | | | | | | | |
| 95.4 | 3.1 | 0.3 | -- | 1.2 | -- | 1.3 | 101.0 | 1 | -- | 1 | -- | 4.4 |
| | | | | | Concentrator and Smelter | | | | | | | |
| 82.7 | 8.2 | 0.4 | 3.9 | 2.4 | -- | 1.6 | 1.3 | 1 | (d) | 1 | -- | 1.6 |
| 95.0 | -- | 5.0 | | | -- | 1.2 | -- | -- | -- | -- | -- | 1.2 |

Continued on following page.

TABLE 9. WATER USES AND RECIRCULATION PRACTICE IN COPPER PRODUCING MINES AND PLANTS (Continued)

| Percent of New Water | | | | | | Use Ratio[(a)] by Process | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Process | Cooling | Boiler Feed | Air Pollution Control | Sanitary | Other | Process | Cooling | Boiler Feed | Air-Pollution Control | Sanitary | Other | Overall |
| | | | | | | **Smelter** | | | | | | |
| 0.6 | 51.5 | 1.8 | 45.0 | 1.1 | -- | 1 | 1.6 | 2.2 | 1 | 1 | -- | 1.7 |
| 0.7 | 80.7 | 2.0 | 13.3 | 3.3 | -- | 1 | 12.8 | 10.1 | 1 | 1 | -- | 10.9 |
| 56.0 | 30.9 | 4.3 | 6.7 | 2.1 | -- | 1.6 | 3.8 | 1 | 14.0 | 1 | — | 3.1 |
| | | | | | | **Refinery** | | | | | | |
| 0 | 74.9 | 24.5 | -- | 0.6 | -- | -- | -- | -- | -- | -- | — | 8.1 |
| 7.6 | 59.8 | 20.4 | | 12.2 | -- | -- | -- | -- | -- | -- | -- | — |
| 81.3 | 8.3 | 8.0 | 0.7 | 1.7 | -- | 1.0 | 38.4 | 1.2 | 1 | 1 | -- | 4.1 |
| 61.4 | 16.7 | 10.0 | -- | 11.7 | -- | 1.0 | 2.3 | 1.0 | --- | 1 | -- | 1.2 |
| 49.2 | — | 25.4 | -- | 25.4 | -- | -- | -- | -- | -- | -- | — | 1 |
| | | | | | | **Smelter and Refinery** | | | | | | |
| 1.4 | 92.3 | 4.7 | >0.1 | 1.6 | -- | 6.4 | 4.9 | 1 | 1 | 1 | — | 3.55 |
| 1.8 | 94.2 | 1.6 | 1.9 | 0.5 | -- | 1 | 1.2 | 1 | 3.3 | 1 | — | 1.22 |

(a) Use Ratio = Total Use ÷ New Water Use; 1 signifies no recycling

(b) Water transferred to leaching.

(c) Combined process and cooling.

(d) Recirculated to concentrator.

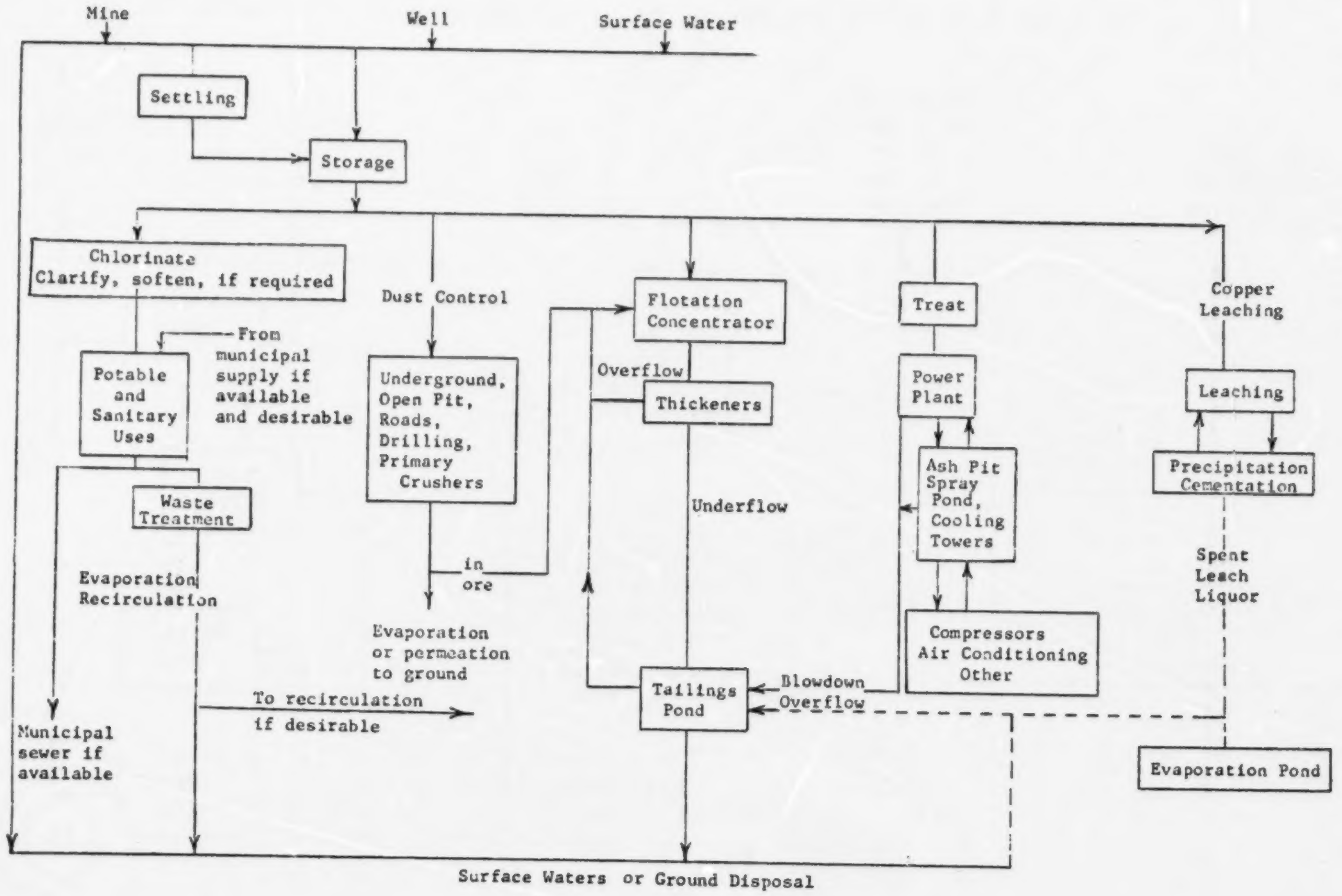

Mine
Well
Surface Water
Settling
Storage
Chlorinate Clarify, soften, if required
Potable and Sanitary Uses
From municipal supply if available and desirable
Waste Treatment
Evaporation Recirculation
Municipal sewer if available
To recirculation if desirable
Dust Control
Underground, Open Pit, Roads, Drilling, Primary Crushers
in ore
Evaporation or permeation to ground
Flotation Concentrator
Overflow
Thickeners
Underflow
Tailings Pond
Blowdown
Overflow
Treat
Power Plant
Ash Pit Spray Pond, Cooling Towers
Compressors Air Conditioning Other
Copper Leaching
Leaching
Precipitation Cementation
Spent Leach Liquor
Evaporation Pond
Surface Waters or Ground Disposal

FIGURE 8. GENERALIZED WATER FLOW DIAGRAM FOR MINE-CONCENTRATOR OPERATION

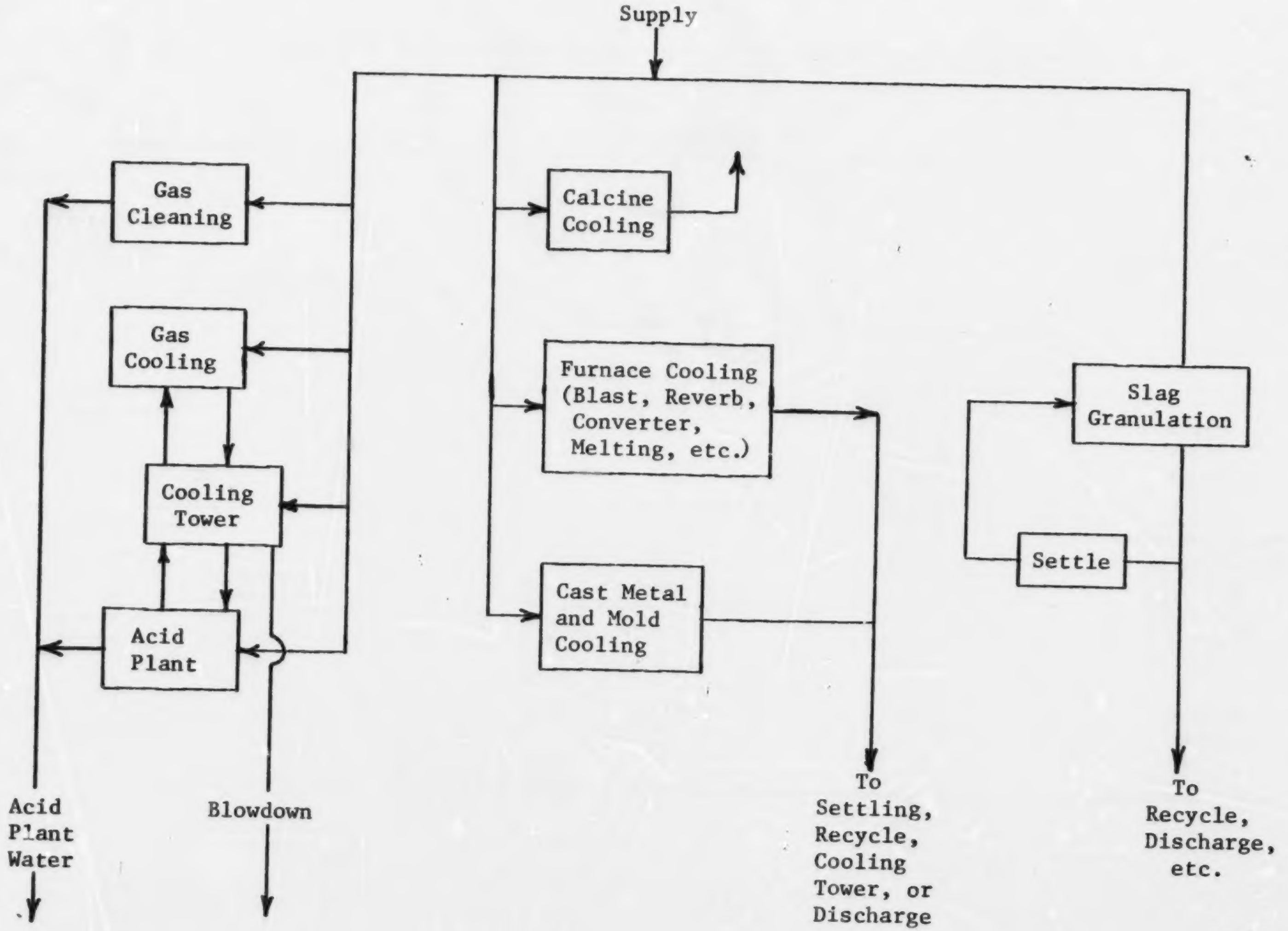

Supply
Gas Cleaning
Gas Cooling
Cooling Tower
Acid Plant
Calcine Cooling
Furnace Cooling (Blast, Reverb, Converter, Melting, etc.)
Cast Metal and Mold Cooling
Slag Granulation
Settle
Acid Plant Water
Blowdown
To Settling, Recycle, Cooling Tower, or Discharge
To Recycle, Discharge, etc.

FIGURE 9. GENERALIZED WATER-FLOW DIAGRAM FOR SMELTER-TYPE OPERATION

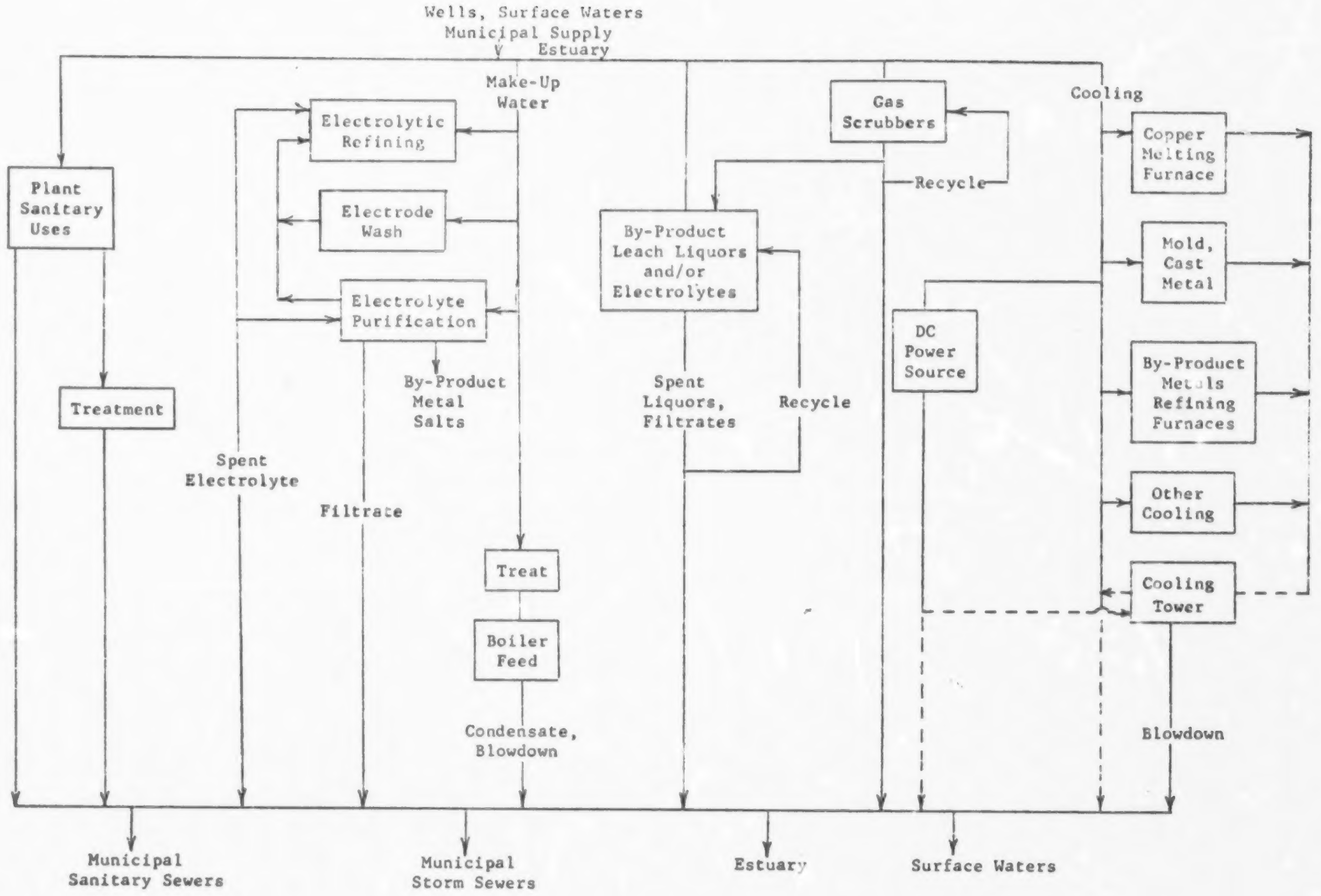


FIGURE 10. GENERALIZED WATER FLOW DIAGRAM FOR ELECTROLYTIC REFINERY

pond loop and reused.

A water loop characteristic of the copper industry is the leaching operation where the large quantities of water, really dilute acid solution, are recirculated between an ore dump and a copper-precipitation plant. Losses to evaporation and ground seepage must be made up with intake water, which may range in quality down to sewage-plant effluent. Spent leach liquor no longer usable owing to the buildup of various salts may be discharged, evaporated, or sent to a tailings pond. Mine-concentrator operations, particularly in the arid sections of the west, often employ complete recirculation with no discharge to surface waters.

Figure 9 is a generalized flowsheet showing the use of water in smelters. These may be associated with mine and concentrator and utilize the same water sources, sanitary circuit, and the tailings pond for discharge, or they may be a separate installation. The common features of the water circuits of a smelter are the manifold cooling functions: spray cooling of calcine in the roasting or sintering operations, where water is mostly lost to evaporation or stays in the material; the cooling of furnace components (doors, shells, etc.); and the cooling of the cast metal product and the casting molds. Furnace cooling requires no contact of the water with the material being processed, and cooling of solidified metal and molds generally results only in the pickup of mold-dressing materials (oils or silica-base compounds). This cooling water may be settled to remove suspended solids and recycled or discharged. In some plants, molten slag from the furnaces is granulated with water jets, the slurry dewatered, and the water settled and either recycled or discharged.

Smelting operations may include sulfuric acid plants. Water is used in these in a number of ways. Water scrubbers are used to remove dusts and fumes from sulfur dioxide gas streams from roasters and converters before admission to the sulfuric acid plant. Water is used to dilute the sulfuric acid product to the desired strength. It is used to cool reactors and machinery. Acid plants produce discharges of cooling-tower blowdown and "acid plant waters" from the sumps of the gas cleaning or conditioning steps. The locations of smelters vary from deserts to seacoasts and thus sources of supply and types of receivers may include independent systems, municipal systems, or estuarine waters, or combinations thereof. In some installations, slags are granulated by shock cooling with water before disposal or recirculation.

The pattern of water usage and waste treatment or disposal in electrolytic refineries is depicted in Figure 10. Make-up water is used for the preparation of electrolytes for both the primary product and, in many cases, precious or other metal by-products as well as the preparation of solutions for various leaching and chemical operations. Wet gas scrubbers may use water for either or both of the functions of air-pollution control and by-product recovery. Virtually all electrolytic refineries employ melting, refining, and casting operations to produce salable forms of the primary and by-product metals, and require use of cooling water for furnace components, cast metal, molds, etc. When these are located near seacoasts, cooling is accomplished with salt water, usually pumped from and returned to estuaries. Cooling is also required for the characteristic electrical equipment such as transformers, rectifiers, generators, etc. Steam generation is also required for controlling the temperature of the electrolytic baths. The discharges from electrolytic refineries are many and varied, as are the disposal techniques and types of receivers.

## Specific Sources of Waste Water

Specific sources of waste water in the copper industry are as follows:

1. Water-treatment wastes, including filter backwash, sludges from primary settling and ion-exchange regeneration solutions.

2. Sanitary wastes.

3. Indirect and direct cooling water from the cooling of furnaces, machinery, casting operations, etc. Generally, such water is recirculated to cooling towers or spray ponds for reuse, and is eventually discharged as blowdown. Some plants, notably smelters and refineries located near large bodies of water such as the sea, may use once-through cooling water.

4. Process wastes including mine drainage, flotation-plant discharges, discarded leaching solutions, scrubber water, smelter waste water, discarded electrolyte from refineries, sanitary waste, clean-up water, etc. Often these may be combined in tailings ponds for treatment and recirculation.

5. Boiler and power plant wastes including boiler blowdown and ash-pit overflow.

Data on the quantity of these individual waste streams were not available to this study. Some data on the characteristics of such wastes were obtained however. Table 10 shows the composition of raw waste to tailings ponds and of tailings-ponds effluents for several mine-concentrator combinations. Table 11 gives similar data for several operations involving mines, concentrators, and smelters. Table 12 shows compositions of waste streams from copper smelters and refineries.

The methods of waste treatment used in the copper industry as revealed by this study are shown in Table 13.

TABLE 10. COMPOSITIONS OF WASTE WATERS FROM MINE AND CONCENTRATOR OPERATIONS

(All analyses in mg/l)

| | Raw Waste to Tailings Ponds | | | | |
|---|---|---|---|---|---|
| Components[a] | Discharge from Concentrator | Plant Drain A | Plant Drain B | | Tailings Pond Effluent |
| As | 0.01 | 0.09 | 0.03 | | 0.006 |
| BOD | 5.8 | 164 | 50 | | -- |
| Cd | 0.01 | -- | -- | | nil |
| CN | 0.06 | -- | -- | | |
| Cu | 0.10 | 0.33 | 0.28 | | 0.01 |
| F | 2.9 | 2.1 | 1.3 | | |
| Fe | 0.12 | -- | -- | | 0.05 |
| Mn | 0.08 | -- | -- | 0.8 | nil |
| Pb | 0.005 | -- | -- | 0.18 | 0.02 |
| pH | 7.3 | 7.0 | 6.7 | 7.64 | -- |
| TDS | 3412 | 2310 | 3950 | | -- |
| TSS | 48 | 549 | 53 | | -- |
| Zn | 0.03 | -- | -- | 2.0 | -- |
| COD | -- | 343 | 106 | | -- |
| Coliform | -- | 211,000 | 20,000 | | -- |
| Metal Sulfides | -- | 0.23 | 0.18 | | -- |

(a) BOD = Biological oxygen demand
CN = Free cyanide
TDS = Total dissolved solids
TSS = Total suspended solids
COD = Chemical oxygen demand
Coliform = Bacteria per 100 ml.

TABLE 11. WATER ANALYSES ASSOCIATED WITH COPPER SMELTING OPERATIONS

| Units: | mg/l | | mg/l | | ppm | | | |
|---|---|---|---|---|---|---|---|---|
| Description: | | Tailings Pond | | Tailings Pond | Intakes | | Receiver of Tailings Pond Outlet | |
| Components(a) | Intake | Overflow | Intake | Overflow | Min | Max | Min | Max |
| As | <0.01 | <0.01 | -- | -- | -- | -- | -- | -- |
| BOD | 1.6 | 1.0 | -- | -- | -- | -- | -- | -- |
| Ca | 14. | 60. | 172. | -- | 24. | 205. | 136. | 144. |
| Cd | <0.005 | <0.005 | -- | -- | -- | -- | -- | -- |
| Cl | 3.0 | 120. | 195. | 200. | 1. | 17. | 22. | |
| CN | -- | -- | -- | -- | -- | -- | -- | -- |
| COD | -- | -- | -- | -- | -- | -- | -- | -- |
| Cu | <0.010 | <0.010 | -- | -- | 0.04 | 0.15 | 0.05 | |
| F | 0.16 | 0.35 | -- | -- | -- | -- | -- | -- |
| Fe | 0.03 | 0.1 | -- | -- | -- | -- | -- | -- |
| Hardness | 35. | 151. | 540. | -- | 94. | 600. | 700. | 736. |
| HCl | -- | -- | -- | -- | -- | -- | -- | -- |
| Hg | <0.001 | <0.001 | -- | -- | -- | -- | -- | -- |
| $H_2SO_4$ | -- | -- | -- | -- | -- | -- | -- | -- |
| K | 0.5 | 11.0 | -- | -- | -- | -- | -- | -- |
| Mg | 3.7 | 0.3 | 26.4 | -- | 8. | 22. | 92. | 110. |
| Mn | -- | -- | -- | -- | -- | -- | -- | -- |
| $(M)S_2$ | -- | -- | -- | -- | -- | -- | -- | -- |
| Na | 1.5 | 65.0 | -- | --- | 2. | 19. | 25. | 27. |
| Ni | <0.010 | <0.010 | -- | -- | -- | -- | -- | -- |
| $NO_3$-N | 0.25 | 0.75 | -- | -- | -- | -- | -- | -- |
| Oxygen (dissolved) | 8.7-13.1 | 8.7-12.0 | -- | -- | -- | -- | -- | -- |
| P (total) | 0.01 | 0.12 | -- | -- | -- | -- | -- | -- |
| Pb | <0.005 | <0.005 | -- | -- | -- | -- | -- | -- |
| pH | 8.2 | 10.0 | 8.8 | 7.9 | 7.2 | 8.5 | 7.9 | 7.9 |
| Se | -- | -- | -- | -- | -- | -- | -- | -- |
| $SiO_2$ | -- | -- | -- | -- | 7. | 22. | 20. | |
| $SO_4$ | 3.0 | 1.5 | 750. | 90.5 | 5. | 740. | 309. | 475. |
| TDS | 60. | 400. | -- | 102.8 | 140. | 1100. | 1050. | 1300. |
| TSS | 1-35 | 10-20 | -- | 14.0 | -- | --- | -- | -- |
| Total Acidity | -- | -- | -- | -- | -- | -- | -- | -- |
| Zn | <0.005 | <0.005 | -- | -- | -- | -- | -- | -- |

(a) BOD = Biological oxygen demand
CN = Free cyanide
TDS = Total dissolved solids
TSS = Total suspended solids
COD = Chemical oxygen demand.

## TABLE 12. COMPOSITION OF WASTE STREAMS FROM COPPER SMELTERS AND REFINERIES

(Analyses in mg/l)

| Components[a] | Smelter<br>Acid Plant Water | Smelter<br>Combined Plant Waste | Electrolytic Refineries<br>I<br>Intake | <br>I<br>Discharge | <br>II<br>Combined | <br>III | <br>IV |
|---|---|---|---|---|---|---|---|
| As | <5 | 22.1 | -- | -- | -- | -- | 0.55 |
| BOD | -- | 211 | 10 | 70 | -- | -- | -- |
| Cd | -- | 0.6 | -- | -- | <0.1 | -- | -- |
| COD | -- | 457 | -- | -- | -- | -- | -- |
| Cu | <9 | 7.4 | 0.07 | 0.15 | 50-100 | 0.35 | 2.8 |
| Metal Sulfides | -- | 11.7 | -- | -- | -- | -- | -- |
| Pb | <5 | 7.2 | -- | -- | 1 | 0.05 | -- |
| pH | 2.5-3.0 | 1.9 | 7.4 | 7.7 | 1-2 | 6.1 | 7.6 |
| Se | -- | 0.7 | -- | -- | 26,000 | -- | 0.7 |
| $SO_4$ | -- | 1716 | -- | -- | 26,000 | -- | -- |
| TSS | -- | 167 | -- | -- | -- | 48 | -- |
| TDS | -- | -- | -- | -- | 2-30,000 | 1024 | -- |
| Zn | <6 | 7.3 | 0.3 | 0.4 | -- | -- | -- |
| Fe | -- | -- | 0.2 | 1.00 | 50 | -- | -- |
| Ni | -- | -- | <.1 | <0.1 | 10-20 | -- | -- |
| Cr | -- | -- | -- | -- | -- | <0.03 | -- |
| Hg | -- | -- | -- | -- | -- | <0.1 | -- |
| Oil | -- | -- | -- | -- | -- | 10.5 | -- |
| F | -- | -- | -- | -- | -- | -- | 0.6 |

(a) BOD = Biological oxygen demand
CN = Free cyanide
TDS = Total dissolved solids
TSS = Total suspended solids
COS = Chemical oxygen demand.

TABLE 13. WASTE WATER TREATMENT PRACTICES IN THE COPPER INDUSTRY

| Type of Waste | Treatment |
|---|---|
| Mine and Concentrator | Recirculation with no discharge in arid climate; sedimentation in tailings ponds; neutralization, flocculation if required |
| Smelter | Combined with mine and concentrator wastes where possible, recirculation in arid climate |
| Electrolytic Refinery | Practice variable; neutralization, evaporation, precipitation as required |
| Leaching Plants | Recirculation with discarded leach liquor routed to tailings ponds where acid is neutralized |

## Future Waste-Water-Treatment Methods in the Copper Industry

Cooperating respondents in the copper industry indicated that the following steps were either being taken or being seriously considered to improve the quality of waste discharged:

1. Increased recirculation of waste water with the ideal objective of 100 percent reuse

2. Neutralization of waste discharges from tailings ponds when indicated

3. The use of polyelectrolyte flocculants in place of lime to obtain better settling

4. Increased size of settling ponds

5. Neutralization and precipitation of leach solutions now being discarded and reuse of the water in leaching

6. Installation of settling ponds in smelters with provisions for pH and temperature control so that water can be completely recirculated

7. Rerouting of sewer lines in smelters so that wastes with suspended solids burden can be segregated and sent to thickeners or lagoons

8. Isolation and reuse of "clean" water now being discharged to waste by smelters

9. Reduction in the quantity of cooling water now being used in smelters to cool converter hoods by installation of a new system

10. Neutralization of scrubber waters from the gas cleaning step in sulfuric acid plants

11. Reduction of the amount and strength of the waste from electrolytic refineries by recirculating cathode wash water, spills, etc.

12. Investigation of the possibility of deep-well injection in conjunction with some recycling for smelter and refinery wastes.

# SECTION VIII

## THE PRIMARY LEAD AND ZINC INDUSTRIES

### Size and Characteristics

The lead and zinc industries are closely associated. Lead and zinc minerals occur in many major ore bodies in such intimate mixtures that they must be mined together. Most lead ores contain significant quantities of zinc. Similarly, many zinc ores contain economically significant amounts of lead. Even when lead or zinc minerals predominate in a given ore, neither is entirely free of the other and, at some stage of processing, separations must be made. In addition, lead and zinc ores commonly contain other metals, such as copper, bismuth, antimony, gold, and silver, which for technological or economical reasons must be separated from lead and zinc. The processes for treating lead ores, zinc ores, and lead-zinc ores are highly complicated operations interwoven with each other as well as with processes for copper, precious metals, cadmium, etc.

As an example of the interconnection of the lead-zinc industries, Table 14 shows the amounts of lead and zinc recovered from so-called lead mines, zinc mines, lead-zinc mines, and other sources in the country. This table also indicates the geographical distribution of the mining section of the industry. As shown in the table, virtually all of the so-called lead mines produce zinc in an amount averaging, the country over, to about 13 percent of the lead production. The table also shows that most of the designated zinc deposits yield some lead, with two notable exceptions in Tennessee and Pennsylvania. In the designated lead-zinc mines, the recovery of each metal is about equal. In complex ore bodies associated with copper, the ratio of lead to zinc recovery is about 1 to 2.2 and, in the case of the miscellaneous sources, zinc recovery preponderates over lead recovery by more than 2 to 1.

The total number of mine sources of zinc and lead in the United States has been placed at 300. These mines are mostly in the Rocky Mountain and Missouri-Tennessee areas, but minable deposits are scattered in many of the states throughout the country, excluding the Gulf Coast states. Smelters and refineries are similarly widely located. Zinc and lead production in the United States ranks fourth and fifth, respectively, in tonnage, after iron, aluminum, and copper. The industry consists of a large number of individual mining operations, with an associated concentrating facility (usually a flotation process), and a lesser number of smelting and refining operations.

## TABLE 14. PRODUCTION OF LEAD AND ZINC IN THE UNITED STATES IN 1969, BY STATE AND CLASS OF ORE, FROM OLD TAILINGS, ETC., IN TERMS OF RECOVERABLE METALS(1)

(Short tons)

| State | Copper-lead, copper-zinc, and copper-lead-zinc ores | | | All other sources [6] | | | Total | | |
|---|---|---|---|---|---|---|---|---|---|
| | Gross weight (dry basis) | Lead content | Zinc content | Gross weight (dry basis) | Lead content | Zinc content | Gross weight (dry basis) | Lead content | Zinc content |
| Alaska | ----- | ----- | ----- | ----- | ----- | ----- | 50 | 2 | ----- |
| Arizona | 104,084 | 33 | 8,663 | 20,179,824 | 16 | 278 | 20,287,178 | 217 | 9,039 |
| California | ----- | ----- | ----- | 6,599 | 235 | 8 | 111,051 | 2,518 | 3,327 |
| Colorado | 411,175 | 9,316 | 12,274 | 70,155 | 1,328 | 32 | 1,089,979 | 21,767 | 53,715 |
| Idaho | ----- | ----- | ----- | 818,284 | 5,687 | 7,391 | 1,800,126 | 65,597 | 55,900 |
| Kansas | ----- | ----- | ----- | ----- | ----- | ----- | 59,399 | 395 | 1,900 |
| Missouri | ----- | ----- | ----- | ----- | ----- | ----- | 7,873,545 | 355,452 | 41,099 |
| Montana | ----- | ----- | ----- | 78,169 | 1,224 | 4,988 | 93,306 | 1,753 | 6,143 |
| Nevada | 174 | 45 | 6 | 1,735,640 | 153 | 32 | 1,753,549 | 1,420 | 941 |
| New Jersey | ----- | ----- | ----- | ----- | ----- | ----- | 149,920 | ----- | 25,076 |
| New Mexico | ----- | ----- | ----- | 946,516 | 1 | 664 | 1,222,762 | 2,368 | 24,308 |
| New York | ----- | ----- | ----- | ----- | ----- | ----- | 740,825 | 1,686 | 58,728 |
| Oklahoma | ----- | ----- | ----- | (4) | (4) | (4) | 240,998 | 605 | 2,744 |
| Oregon | ----- | ----- | ----- | 212 | (7) | (7) | 212 | (7) | (7) |
| Pennsylvania | ----- | ----- | ----- | ----- | ----- | ----- | 630,587 | ----- | 33,035 |
| South Dakota | ----- | ----- | ----- | 35 | 1 | ----- | 35 | 1 | ----- |
| Tennessee | 1,574,140 | ----- | 9,976 | ----- | ----- | ----- | 5,862,642 | ----- | 124,532 |
| Utah | 117,452 | 5,963 | 3,368 | 54,927 | 680 | 1,557 | 624,566 | 41,332 | 34,902 |
| Virginia | ----- | ----- | ----- | ----- | ----- | ----- | 660,142 | 3,358 | 18,704 |
| Washington | ----- | ----- | ----- | (4) | (4) | (4) | 477,316 | 8,649 | 9,738 |
| Wisconsin | ----- | ----- | ----- | ----- | ----- | ----- | 846,233 | 1,102 | 22,901 |
| Other States | ----- | ----- | ----- | 220,987 | 349 | 5,906 | 723,424 | 791 | 26,392 |
| Total | 2,207,025 | 15,357 | 34,287 | 24,111,348 | 9,674 | 21,456 | 45,247,845 | 509,013 | 553,124 |
| Percent of total lead-zinc | ----- | 3 | 6 | ----- | 2 | 4 | ----- | 100 | 100 |

---

[1] Lead and lead-zinc ores combined to avoid disclosing individual company confidential data.
[2] Zinc and lead-zinc ores combined to avoid disclosing individual company confidential data.
[3] Includes minor amount of lead tailings comingled with ore at mill; excludes barium sulfate ore.
[4] Includes lead recovered from barium sulfate ore.
[5] Ore from "Other Sources" combined with zinc ore to avoid disclosing individual company confidential data.
[6] Lead and zinc recovered from copper, gold, silver, fluorspar, and uranium ores, and from smelter slags, mill tailings, and miscellaneous cleanups.
[7] Less than ½ unit.

## Geographic Distribution

The names, ownerships, locations, and ore-production figures of selected major lead and zinc producing mines, as gathered in a survey by the lead and zinc industry in 1968 and published in 1970(12), are shown in Table 15. Tables 16 and 17 show similar data for zinc-producing plants and lead smelters and refineries, respectively.

The geographic distribution of the mining sources and of the smelters and refineries is shown on the map in Figure 11. Table 17, previously referred to, lists the lead and zinc production by states, for 1969, from various ore sources. As may be gathered from the table, the states east of the Mississippi River produced about 60 percent of the zinc, while western states produced 36 percent, and the Kansas-Oklahoma area produced 4 percent.

In contrast, mines west of the Mississippi produced 96 percent of the lead ores, with the most important lead-producing areas being the Summit Valley region in Montana, the Metaline Falls area in Washington, the Upper San Miguel region in Colorado, and the rapidly developing New Lead Belt in southeastern Missouri.

Table 18 lists salient economic statistics for that phase of the lead-zinc industry concerned with smelting and refining for the year 1967.(6) Similar data for the mining and milling phases of the industry were not available to this study. It has been stated, however, that production personnel engaged in mining and milling of lead and zinc in 1968 amounted to about 10,000. Table 19 lists the major uses of lead and zinc.

## Projected Growth

In spite of current fluctuations in price, plant closings, and uncertainty of the future market for tetraethyl lead, the Bureau of Mines prediction for the annual rate of growth of the lead and zinc industries ranges from 1.2 to 3.4 percent for both metals.(8) The 1968 base production figures and predicted high and low figures for the year 2000 were given as follows:

| | Zinc | Lead |
|---|---|---|
| 1968 Primary Production, short tons | 529,000 | 359,000 |
| Year 2000 Primary Production Range, short tons: | | |
| High | -- | 1,120,000 |
| Low | 786,000 | 520,000 |
| 1968-2000 Growth Rate, percent | | |
| High | 3.3 | 3.4 |
| Low | 1.2 | 1.8 |

TABLE 15. LEAD AND ZINC MINES REPORTED BY 1968 INDUSTRY SURVEY(12)

| Company Name | Name of Mine | Location of Mine | Metals Contained in Ore | 1968 Ore Production, short tons |
|---|---|---|---|---|
| American Smelting and Refining Co. | Page | Idaho | Pb, Zn, Ag | 86,560 |
| American Zinc Co.[a] | New Market | Tennessee | Zn, Pb | 747,430 |
| Ditto | Calhoun | Washington | Zn, Pb | 298,030 |
| " | Blackstone | Wisconsin | Zn, Pb | 8,000 |
| " | Champion | Wisconsin | Zn | 133,815 |
| " | Bearhole | Wisconsin | Zn | 2,910 |
| " | Thompson-Temperly | Wisconsin | Zn | 83,700 |
| " | Mascot No. 2 | Tennessee | Zn | 530,930 |
| " | Young | Tennessee | Zn | 1,040,680 |
| " | N. Friends Station | Tennessee | Zn | 105,670 |
| " | Coy | Tennessee | Zn | 151,480 |
| " | Immel | Tennessee | Zn | 252,040 |
| Bunker Hill Co. | Bunker Hill | Idaho | Ag, Pb, Zn | 387,120 |
| Ditto | Crescent | Idaho | Ag | 28,530 |
| " | Star | Idaho | Ag, Pb, Zn | 189,540 |
| Callahan Mining Corp. | Penobscot | Maine | Zn | 111,760 |
| Canyon Silver Mines | Canyon Silver | Idaho | Ag, Pb, Zn | 2,310 |
| Cyprus Mines Corp. | Bruce | Arizona | Zn | |
| Day Mines Inc. | Dayrock | Idaho | Ag, Pb, Zn | 26,085 |
| Dresser Industries Inc./ Cominco American | Magmont | Missouri | Pb | 127,730 |

Continued on following page.

TABLE 15. LEAD AND ZINC MINES REPORTED BY 1968 INDUSTRY SURVEY (continued)

| Company Name | Name of Mine | Location of Mine | Metals Contained in Ore | 1968 Ore Production, short tons |
|---|---|---|---|---|
| Eagle-Picher Industries Inc. | Blackjack | Illinois | Zn | |
| Ditto | Birkett | Wisconsin | Zn | |
| " | Bautsch | Illinois | Zn | |
| " | Rehm-Bauer | Illinois | Zn | |
| " | Shullsburg | Wisconsin | Zn | |
| " | Hutson | Kentucky | Zn | |
| " | Grace B | Oklahoma | Zn | |
| " | Westside | Oklahoma | Zn | |
| Hand, John | Hand | Montana | Au, Ag, Pb | 2,250 |
| Hecla Mining Co. | Star-Morning | Idaho | Ag, Pb, Zn | 189,540 |
| Ditto | Silver Summit | Idaho | Ag, Cu | 21,890 |
| " | Lucky Friday | Idaho | Ag, Cu, Pb, Zn | 95,720 |
| " | Mayflower | Utah | Ag, Cu, Pb, Zn | 122,100 |
| Idarado Mining Co. | Idarado | Colorado | Zn | 424,010 |
| Ivey Construction Co. | Graysville | Wisconsin | Zn | 19,060 |
| Kennecott Copper Corp. | Burgin | Utah | Ag, Pb, Zn | 199,580 |
| McFarland & Hullinger | Iron King | Arizona | Ag, Cu, Pb, Zn | 101,870 |
| Monte Cristo Mining Corp. | Jubilee | California | Pb, Ag, Au | 1,995 |
| New Jersey Zinc Co. | Austinville | Virginia | Zn | 657,825 |
| Ditto | Hanover | New Mexico | Zn | 181,830 |
| " | Gilman | Colorado | Zn | 256,770 |
| " | Sterling | New Jersey | Zn, Fe, Mn | 156,425 |
| " | Jefferson City | Tennessee | Zn | 464,410 |
| " | Friedensville | Pennsylvania | Zn | 627,830 |
| " | Flat Gap | Tennessee | Zn | 508,100 |
| " | Elmo | Wisconsin | Zn | 213,955 |

Continued on following page.

TABLE 15. LEAD AND ZINC MINES REPORTED BY 1968 INDUSTRY SURVEY (continued)

| Company Name | Name of Mine | Location of Mine | Metals Contained in Ore | 1968 Ore Production, short tons |
|---|---|---|---|---|
| New Market Zinc Co. | New Market | Tennessee | Zn | |
| Osceola Metals Corp. | Osceola | Colorado | Pb, Zn, Cu, Ag, Au | 14,270 |
| Ozark Lead Co. | Ozark Lead | Missouri | Pb, Zn | |
| Ozark-Mahoning Co. | Shaft No. 4 | Illinois | Fluorspar, Zn | 116,705 |
| Ditto | Hill-Ledford | Illinois | Fluorspar, Zn | 66,120 |
| " | Shaft No. 10 | Illinois | Fluorspar, Zn | 57,545 |
| " | Burnett Complex | Illinois | Fluorspar, Zn, Pb | 51,425 |
| " | Taylor | Illinois | Fluorspar, Zn | 59,895 |
| Pend Oreille Mines & Met. Co. | Pend Oreille | Washington | Pb, Zn | |
| St. Joseph Lead Co. | Edwards | New York | Zn | |
| Ditto | Balmat | New York | Zn | |
| " | Federal | Missouri | Pb | |
| " | Indian Creek | Missouri | Pb | |
| " | Viburnum | Missouri | Pb | |
| " | Fletcher | Missouri | Pb | |
| Standard Metals Corp. | Sunnyside | Colorado | Pb, Zn | |
| T. Geo. Inc. | Dobson | Oklahoma | Pb, Zn | 13,325 |
| Tennessee Copper Corp.(b) | Eureka | Tennessee | Cu, Zn | |
| Ditto | Boyd | Tennessee | Cu, Zn | |
| " | Calloway | Tennessee | Cu, Zn | |
| " | Cherobee | Tennessee | Cu, Zn | |

Continued on following page.

TABLE 15. LEAD AND ZINC MINES REPORTED BY 1968 INDUSTRY SURVEY (continued)

| Company Name | Name of Mine | Location of Mine | Metals Contained in Ore | 1968 Ore Production, short tons |
|---|---|---|---|---|
| Tongaha Mining Co. | Piokee | Oklahoma | Pb, Zn | 26,660 |
| United Park City Mines Co. | United Park City | Utah | Pb, Zn, Ag | |
| U.S. Steel-Corp. | Zinc Mine | Tennessee | Zn | |
| West Hill Exploration Inc. | Darwin | California | Ag, Pb, Zn | 57,110 |

(a) During the preparation of this report, American Zinc Co. has been reorganizing with some operations being sold to American Smelting and Refining. Specific dispositions are uncertain at this time.

(b) Now operated as part of Cities Service Corp.

TABLE 16. ZINC-PRODUCING PLANTS IN THE UNITED STATES

| Company | Location of Plant | Type of Plant | Annual Capacity (Zinc), short tons | By-Products |
|---|---|---|---|---|
| American Smelting and Refining Co. | Amarillo, Texas | Horizontal Retort | | Cd |
| Ditto | Corpus Christi, Texas | Electrolytic | 89,950 | Cd |
| American Zinc Co. | Dumas, Texas | Horizontal Retort | 56,280 | |
| Ditto | Monsanto, Illinois | Electrolytic | 83,820 | |
| Anaconda Company | Great Falls/Anaconda, Montana | Electrolytic | 251,460 | Cd, Cu, In, Pb |
| Bunker Hill Co. | Bunker Hill, Idaho | Electrolytic | 105,480 | Cd |
| Eagle Picher Ind. Inc. | Henryetta, Oklahoma | Horizontal Retort/ Waelz | 39,915 | |
| Ditto | Galena, Kansas | Roasting Only | 99,790 | Cd |
| Matthiessen & Hegeler Zinc Co.[(a)] | LaSalle, Illinois | Horizontal Retort/ Waelz | 31,930 | Au, Ag, Cd, Pb |
| Ditto | Meadowbrook, West Virginia | Vertical Retort | 44,910 | Se |
| National Zinc Co. | Bartlesville, Oklahoma | Horizontal | 62,650 | Cd |
| New Jersey Zinc Co. | Palmerton, Pennsylvania | Vertical Retort | 117,755 | Cd, In, Pb |
| Ditto | Depue, Illinois | Vertical Retort | 69,855 | In, Pb |
| St. Joseph Minerals Corp. | Monaca, Pennsylvania | | 199,580 | Cd, Hg |

(a) During the preparation of this report, preliminary reports have been seen indicating plant closures at Depue and Meadowbrook and the transfer of some New Jersey Zinc Co. holdings to American Smelting and Refining Co. Final specific dispositions are uncertain at this time.

TABLE 17. LEAD SMELTERS AND REFINERIES IN THE UNITED STATES

| | Smelters | | Refineries | | | |
|---|---|---|---|---|---|---|
| Company | Location | Annual Capacity (Lead Bullion), short tons | Location | Type of Refining | Annual Capacity, (Refined Lead), short tons | By-Product |
| American Smelting & Refining Co. | East Helena, Montana | 107,770 | -- | -- | -- | -- |
| ditto | El Paso, Texas | 107,770 | -- | -- | -- | -- |
| " | Glover, Missouri | 89,815 | Glover, Missouri | Pyro | 89,815 | Au, Ag |
| " | -- | -- | Omaha, Nebraska | Pyro | 179,630 | Au, Ag, Bi, Sb |
| Bunker Hill Co. | Kellogg, Idaho | 124,340 | Bunker Hill, Idaho | Pyro | 122,340 | Au, Ag, Cd, Cu, Sb |
| International Smelting & Refining Co. | Tooele, Utah | 65,860 | -- | -- | -- | -- |
| Missouri Lead Operating Co. | Boss, Missouri | 99,790 | Boss, Missouri | Pyro | 99,790 | Ag, Cu |
| St. Joseph Lead Co. | Herculaneum, Missouri | 224,525 | Herculaneum, Missouri | Pyro | 220,125 | Ag |
| U. S. Smelting, Refining & Mining Co. | -- | -- | East Chicago, Indiana | Electro | 39,915 | -- |

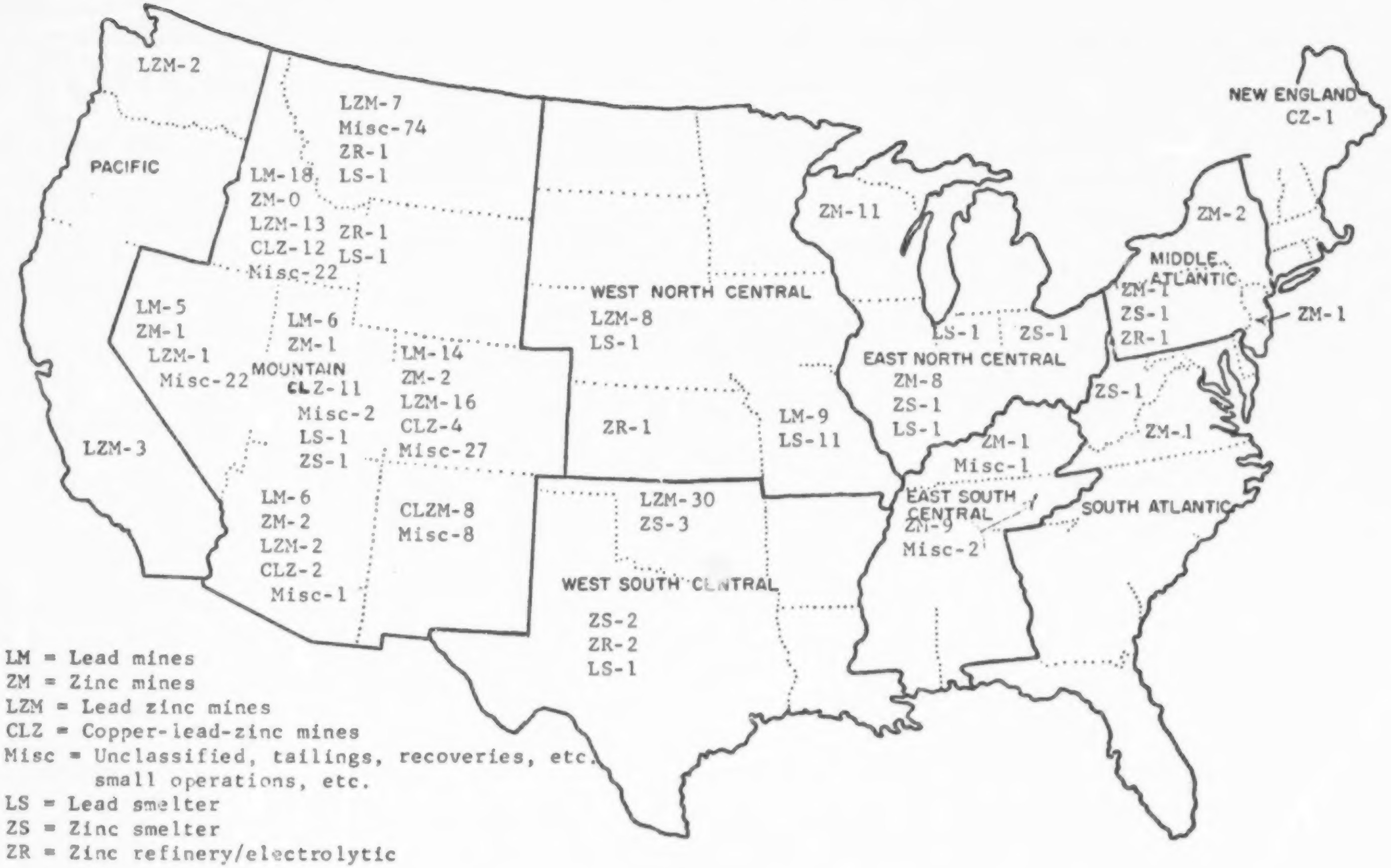


FIGURE 11. GEOGRAPHICAL DISTRIBUTION OF LEAD AND ZINC MINES IN THE UNITED STATES
(U. S. Bureau of Mines Data, Minerals Yearbook, 1969)

TABLE 18. SELECTED ECONOMIC STATISTICS FOR THE PRIMARY ZINC AND LEAD INDUSTRIES (1967)(a)

| | Zinc | Lead |
|---|---|---|
| Number of Employees | 8,100 | 2,700 |
| Payroll, millions of dollars | 57.8 | 18.9 |
| Capital Expenditures, millions of dollars | 25.8 | 18.5 |
| Materials Consumed | | |
| Ores, Concentrates, short tons | 1,757,300 | 1,002,600 |
| Delivered Cost, millions of dollars | 147.5 | 152.8 |
| Cost of All Other Materials and Supplies, millions of dollars | 15.9 | 109.8 |
| Cost of Purchased Fuel and Electrical Energy, millions of dollars | 22.9 | 7.1 |
| Product Primary Refined Metal, short tons | 1,037,700 | 379,894 |
| Value, millions of dollars | 339.1 | 106.37 |

(a) For smelting and refining only; does not include mining.(6)

TABLE 19. CONSUMPTION PATTERN OF LEAD AND ZINC IN 1968(2)

(Short Tons)

| | Lead | Zinc |
|---|---|---|
| Construction | -- | 340,000 |
| Metal Products | 364,250 | -- |
| Transportation | -- | 400,000 |
| Storage Batteries | 513,703 | 50,000 |
| Electrical Equipment | -- | 210,000 |
| Pigments | 107,258 | 220,000 |
| Plumbing and Heating | -- | 240,000 |
| Chemicals | 262,526 | -- |
| Machinery | -- | 160,000 |
| Miscellaneous | 23,106 | 141,000 |
| Pigments and Compounds | -- | 220,000 |
| Unclassified | 17,924 | -- |
| Total | 1,288,767 | 1,761,000 |

The 1968 production figures used here are metal contents of domestic mined ore, which are supplemented by imports of ore and metal and most importantly by recovery of metal values from secondary (scrap) metal.

## Raw Materials and Processes

As an aid in understanding the somewhat involved nature of the processes discussed below, the following discussion is numerically keyed to the diagram in Figure 12.

The ore minerals of lead and zinc are listed in Table 20.

TABLE 20. ORE MINERALS OF LEAD AND ZINC(13)

| Mineral | Chemical Composition | Remarks |
|---|---|---|
| | Lead | |
| Galena | $PbS$ | Principal ore mineral |
| Cerussite | $PbCO_3$ | Results of weathering of galena; may occur in minor amount in galena deposits |
| Anglesite | $PbSO_4$ | Ditto |
| | Zinc | |
| Sphalerite | $ZnS$ | Principal ore mineral in U.S. |
| Franklinite | $(Zn, Mn)O \cdot Fe_2O_3$ | Important ore mineral in New Jersey; minor in rest of U.S. |
| Zincite | $ZnO$ | Ditto |
| Willemite | $Zn_2SiO_4$ | " |
| Gaslarite | $ZnSO_4 \cdot 7H_2O$ | Unimportant |
| Calamine | $Zn_4Si_2O_7(OH)_2 \cdot H_2O$ | Unimportant |

These minerals occur in a wide variety of ore types, grades, and associations with each other and with the ore minerals of copper, silver, gold, and manganese, and nonmetallics such as fluorite. Table 21 exemplifies the ranges encountered in United States ores, the associated ore minerals, and typical gangue rock.

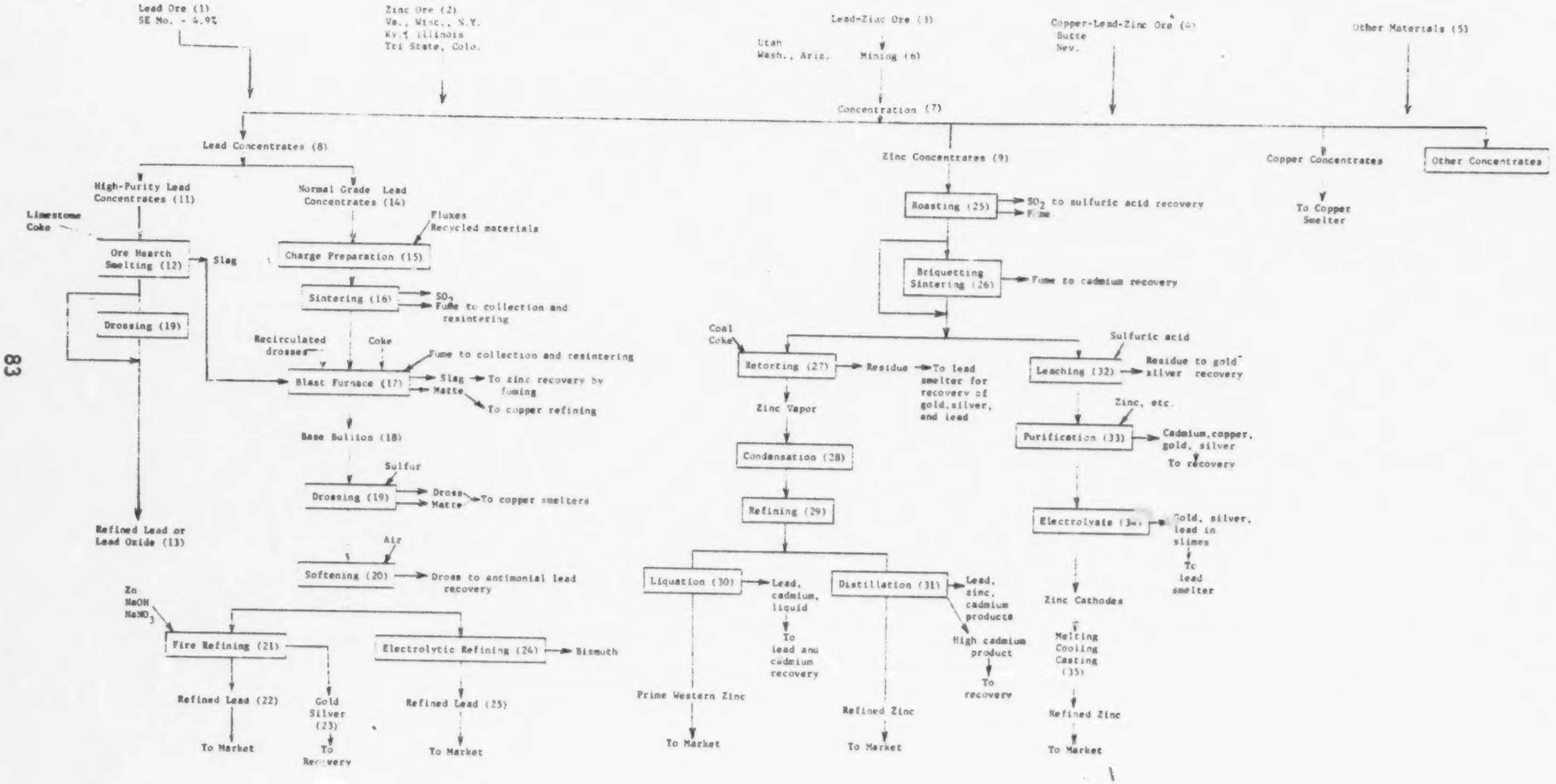


FIGURE 12. DIAGRAM OF OPERATIONS IN LEAD AND ZINC PRODUCTION

TABLE 21. APPROXIMATE GRADE AND ASSOCIATION OF LEAD-ZINC ORES IN THE UNITED STATES

| Region | Approximate Grade |  |  |  |  |  |  | Ore Minerals | Gangue Minerals |
|---|---|---|---|---|---|---|---|---|---|
|  | Cu, % | Pb, % | Zn, % | Mn, % | $CaF_2$, % | Au oz/ton | Ag oz/ton |  |  |
| Va. | -- | 1 | 5 | -- | -- | -- | -- | Galena, sphalerite | Limestone, dolomite |
| Ky.-Ill. | -- | 0.2 | 1-2 | -- | Major | -- | -- | Fluorite, galena, sphalerite | Limestone |
| Wis.-Ill. | -- | 0.3-1.0 | 3-7 | -- | -- | -- | -- | Sphalerite, galene | Marcusite, limestone, dolomite |
| N.Y. | -- | 0.15-0.3 | 3-9 | -- | -- | -- | -- | Sphalerite, galena | Limestone |
| N.J. | -- | -- | -- | -- | -- | -- | -- | Zincite, willemite, franklinite |  |
| SE Mis. | -- | 2-4 | Insignificant | -- | -- | -- | -- | Galena | Marcasite, siegenite, chalcopyrite, dolomite |
| TriState (Mo.,Kan., Okla.) | -- | 0.3 | 2.0 | -- | -- | -- | -- | Galena, sphalerite | Limestone |
| Idaho | Tr-0.6 | 2-10 | 2-10 | -- | -- | -- | 1-30 | Galena, sphalerite, tetrahedrite, pyrite | Quartz, siderite, calcite, dolomite, basite |
| Utah | 0.4 | 8 | 5 | -- | -- | 0.2 | 3-7 | Galena, sphalerite, chalcopyrite, bornite, tetrahedrite | Quartz, feldspar, shale, limestone |
| Wash. | 0.1 | 1.5 | 3 | -- | -- | -- | 0.5 | -- | -- |
| Col. | 0.7 | 3 | 3 | -- | -- | 0.1 | 2-3 | Chalcopyrite, galena, sphalerite, tetrahedrite | Limestone |
| Ariz. N. Mex. | 0.6 | 3 | 7 | -- | -- | 0.1 | 2-3 | Chalcopyrite, etc., galena, sphalerite, tetrahedrite | Limestone, etc. |
| Nev. | -- | By-product | By-product | -- | -- | -- | Principal | Tetrahedrite, galena, sphalerite | -- |
| Calif. | -- | -- | -- | -- | -- | -- | -- | Galena, sphalerite, cerussite, anglesite | -- |
| Tenn. | -- | Low | 2-6 | -- | -- | -- | -- | Sphalerite | Limestone |
| Mont. | Major | (a) | (a) | Major | -- | -- | --- | Chalcopyrite, etc., sphalerite, galena, rhodocrosite | Quartz, feldspar, etc. |

(a) These ores generally contain zinc and lead in minor amounts, usually in the ratio of 5 parts zinc to 1 part lead.

The ores of lead and zinc may be arbitrarily classified according to their principal mineral values. The so-called lead (1) ores, in which lead is a major component and zinc minor, are best exemplified by the ores of southeastern Missouri in which lead is almost exclusively the major metal value. The so-called "lead ores" also occur in many of the Western states and production data for "lead ores", as opposed to zinc ores, lead-zinc ores, etc., are annually published by the Bureau of Mines. These lead ores customarily contain economically significant quantities of zinc, copper, gold, silver, etc.

The so-called zinc ores (2) occur mostly east of the Mississippi (Virginia, Wisconsin, New York, Kentucky, Illinois). Some are found in states west of the Mississippi (Colorado, Missouri, Kansas, Oklahoma). The zinc ores almost always contain significant quantities of lead, with zinc greatly preponderating over lead.

The lead-zinc ores (3) in which lead and zinc both occur in significant quantity and in which copper is not the major mineral value, with neither lead nor zinc greatly preponderating over the other, are found in the West and Southwest and usually contain copper and precious metals.

The so-called copper-lead-zinc ores (4) are also limited to western deposits and are considered to be those ores which yield economically important quantities of copper.

Lead and zinc are also recovered from other ores (5) and materials such as gold and silver ores, tailings piles, etc. These are exclusively western sources.

The above classifications are used by the United States Bureau of Mines in reporting annual data of the lead-zinc industry in the Minerals Year Book.

## Mining (6)

In the United States, almost all lead and zinc ores are mined by underground techniques in contrast to the major open-pit operations of the copper industry. Limited mining of lead and zinc by small open-pit operations has been used in the Tri-state region of Missouri and in Washington. Some zinc mines in the early stages of their development are also mined by open-pit methods. Underground methods most commonly used for lead and zinc mining include block-caving, cut and fill (described in the section of this report on copper), room and pillar, and various stoping techniques.

## Concentration (7)

Ores of lead and zinc are always concentrated. Two general methods of concentration are employed.

In the one, called gravity concentration, advantage is taken of the high specific gravity of the lead minerals galena (specific gravity 7) and of the zinc mineral sphalerite (specific gravity 4.7) to separate them from the lighter gangue or nonore materials. Gravity separation is done either by jigging or by float-sink methods in so-called heavy media. Each route requires that the ore first be crushed to a particle size at which the lead and zinc minerals are liberated or "broken free" of gangue or waste material.

In jigging, the ore is crushed to the desired particle size, which may range from 48 mesh up to 3 inches, and transported by water flow through a machine, called a jig, in which the water-ore medium is pulsated vertically as by the action of a diaphragm. Upward pulsations cause the ore particles to rise. After the upward impulse, they settle again, with the heavier minerals such as galena and sphalerite settling faster than the light gangue or waste materials. The operation is so regulated with respect to the frequency and intensity of the upward pulsations that the lead and zinc minerals accumulate in the bottom and may be drawn off as a concentrate. Lighter materials overflow the top. Jigging is an effective means of concentration if the minerals have a specific gravity-difference of 0.5 unit or more, although special treatment in jigs may permit separation of materials exhibiting specific-gravity differences as little as 0.25. Accordingly, if liberation is obtained, it is possible to produce, by jigging, separate lead and zinc concentrates.

The float-sink or heavy-media method consists of feeding the crushed ore to a suspension of ferrosilicon in water, which has an apparent specific gravity of about 3.4. In this operation, heavy minerals, such as galena, sphalerite, pyrite, etc., sink and the lighter gangue minerals remain afloat. The concentrates of heavy minerals are drawn off the bottom of the heavy-media vessel, washed free of ferrosilicon particles, and sent to further processing. Similarly the floating tailings are separated from ferrosilicon by washing and discarded. The ferrosilicon, washed from the concentrates and tailings, is recovered and recirculated to the heavy-media vessel.

Concentrates obtained by jigging or float-sink methods may be treated directly by smelting practices. More often, however, middling products result. Middling products are those in which the ore mineral is still locked or attached to gangue minerals. Middling products are generally ground finer and sent to flotation.

These gravity methods are often used in lead-zinc metallurgy as preconcentration steps to eliminate gangue constituents of the ore.

Gravity methods are particularly suitable for simple lead or lead-zinc ores associated with gangue or waste minerals of low specific gravity. Ores of this type are common in the mines of the Mississippi Valley and the Eastern United States.

Concentration of lead and zinc ores by flotation is the general practice, however. As discussed in the section of this report on copper, flotation is the process whereby mineral particles in a slurry of water are treated with various chemical reagents to control their surface properties so that they are either wettable or nonwettable, i.e., hydrophilic or aerophilic. As with copper, lead and zinc sulfide minerals can, by treatment with small quantities of flotation reagents, be made aerophilic, so that, in a flotation cell system, they will attach themselves to rising bubbles of air and be transported or "ballooned" to a froth on top of the slurry. This froth is mechanically removed and constitutes a "flotation concentrate". The flotation process with lead and zinc ores is quite complex and exhibits many variations depending on the type of ore, the association of minerals within the ore, and the desired grade and recovery levels of lead or zinc concentrate required. By the use of relatively small quantities of conditioning chemicals it is possible to manipulate the surface properties of the different sulfide materials so that high-grade concentrates of lead and of zinc can be produced from even the most complex ores of lead, zinc, copper, etc.

The flotation process is used not only exclusively on many ores, but is also often employed to affect additional recovery and separation of lead and zinc from the products of the gravity separation methods discussed previously.

Table 22 shows typical analyses of lead and zinc concentrates produced by gravity and flotation procedures (8, 9, 10, 10a).

A generalized flowsheet of the flotation process is shown in Figure 13.

## Lead Production

### High-Purity Lead Concentrates (11)

Some of the ores of southeast Missouri, which are almost exclusively lead ores, yield extremely high-grade lead concentrates. Such concentrates may contain 70 percent or more lead, less than 2 percent silica, less than 4 percent iron plus zinc sulfides, and insignificant quantities of precious metals, arsenic, antimony, bismuth, etc. These are suitable for treatment in the ore hearth furnace.

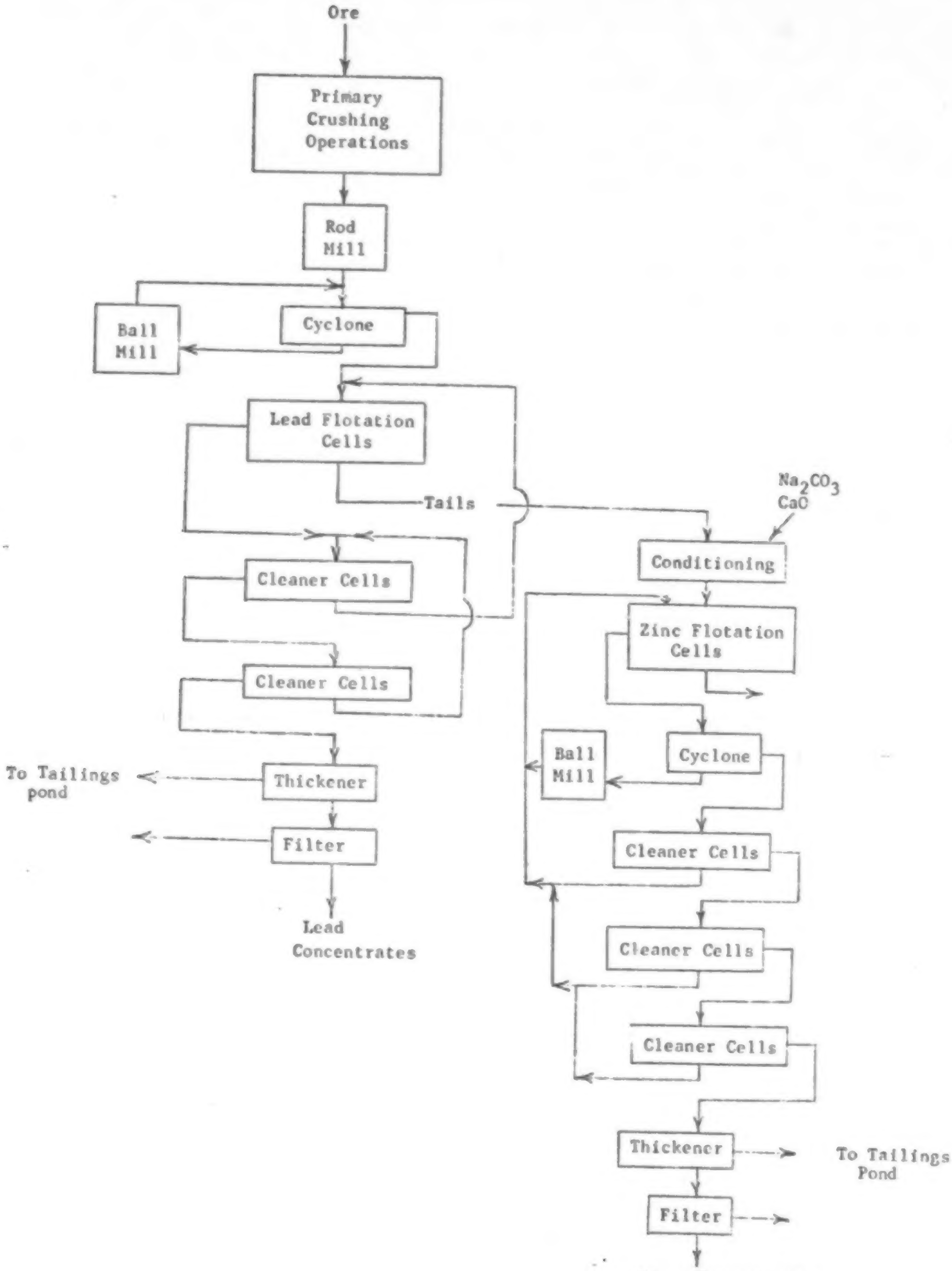


FIGURE 13. PROCESS STEPS IN DIFFERENTIAL FLOTATION OF LEAD-ZINC ORES
(Overflows/froths and underflows/tails indicated diagramatically)

TABLE 22. RANGES OF COMPOSITIONS OF CONCENTRATES IN LEAD AND ZINC METALLURGY (12)

| Constituent | Percent | |
|---|---|---|
| | Lead Concentrates | Zinc Concentrates |
| Pb | 45-60 | 0.85-2.4 |
| Zn | 0-15 | 49.0-53.6 |
| Au | 0-a few oz/ton | -- |
| Ag | 0-50 oz/ton | -- |
| Cu | 0-3 | 0.35 |
| As | 0.01-4.0 | -- |
| Sb | 0.01-2.0 | -- |
| Fe | 1.0-8.0 | 5.5-13.0 |
| Insolubles | 0.5-4.0 | 3.4 |
| CaO | tr$^{(a)}$-3.0 | -- |
| S | 10-30 | 30.7-32.0 |
| Bi | tr$^{(a)}$-0.1 | -- |
| Cd | | 0.24 |

(a) tr = trace.

Ore Hearth Smelting (12)

The modern ore hearth furnace is a mechanically rabbled, shallow basin about 10 feet long, 2 feet wide, and 1 foot deep set under fume hoods and fitted with a cluster of tuyeres for the admission of air across its length. The high-grade ore, mixed with coke and limestone, is spread over the hearth in successive thin layers. Roasting and reduction occur on the hearth. A travelling rake progresses slowly from one end of the basin to the other to keep the charge loose and to break up the slightly caked surface. Melted lead settles to the bottom and is removed through a siphon arrangement to a pot. The slag is removed mechanically and quenched in water. Fumes and dusts are collected for subsequent recovery of lead.

The molten lead product collected in the pot may be cast directly into marketable lead shapes, or may be treated by drossing before casting. Drossing, as is discussed later, consists of cooling the molten lead to a temperature just above its melting point and holding it at that temperature for several hours under an oxidizing atmosphere. As a result, impurities such as copper and antimony collect in the lead oxide layer on the surface and are skimmed off. The high-purity ores of southeast Missouri are said not to require such drossing. Slag, fumes, and dust from the ore hearth furnace may contain from 15 to 40 percent of the lead in the original charge, and are generally re-treated in the lead blast furnace.

The chemical reactions occurring in the ore hearth furnace are:

$$\begin{array}{ccccccc} 2PbS & + & 3O_2 & \rightarrow & 2PbO & + & 2SO_2 \\ \text{Galena} & & \text{(air)} & & \text{Lead oxide} & & \text{Sulfur dioxide} \end{array}$$

$$\begin{array}{ccccccc} PbS & + & 2PbO & \rightarrow & 3Pb & + & SO_2 \; . \\ \text{Galena} & & \text{Litharge} & & \text{Product} & & \text{Sulfur dioxide} \end{array}$$

Refined lead from the ore hearth furnace typically contains about 99.93 percent lead, less than 0.002 percent silver, 0.04 percent copper, 0.015 percent zinc, and traces of iron and bismuth.

The ore hearth furnace was previously employed in some Kansas smelters to produce high-purity lead oxide as well as metallic lead.(14)

## Normal-Grade Lead Concentrates (14)

Most lead-zinc ores will not yield concentrates of the grade required for ore hearth smelting. In addition, these concentrates may contain significant quantities of iron, copper, arsenic, antimony, silver, gold, bismuth, and cadmium, which either must be removed to produce a suitable quality of lead, or which in themselves are worth recovering. For these reasons the blast-furnace path is the most widely used smelting method in the lead industry.

A typical composition of lead concentrate fed to a blast furnace is shown below:

| | Percent | Oz/Ton |
|---|---|---|
| Pb | 32 | -- |
| Zn | 5 | -- |
| S | 10 | -- |
| Fe | 9 | -- |
| Ag | -- | 30-150 |
| Cd | 0.05 | -- |
| Insoluble | 5 | -- |

## Smelting and Refining Processes (15 through 25)

The smelting and refining processes include charge preparation (blending of the concentrate with flux, return products, etc.) (15), sintering (16), blast-furnace smelting (17), and subsequent refining operations to remove and perhaps recover metallic impurities. The unit processes are indicated in Figure 14.

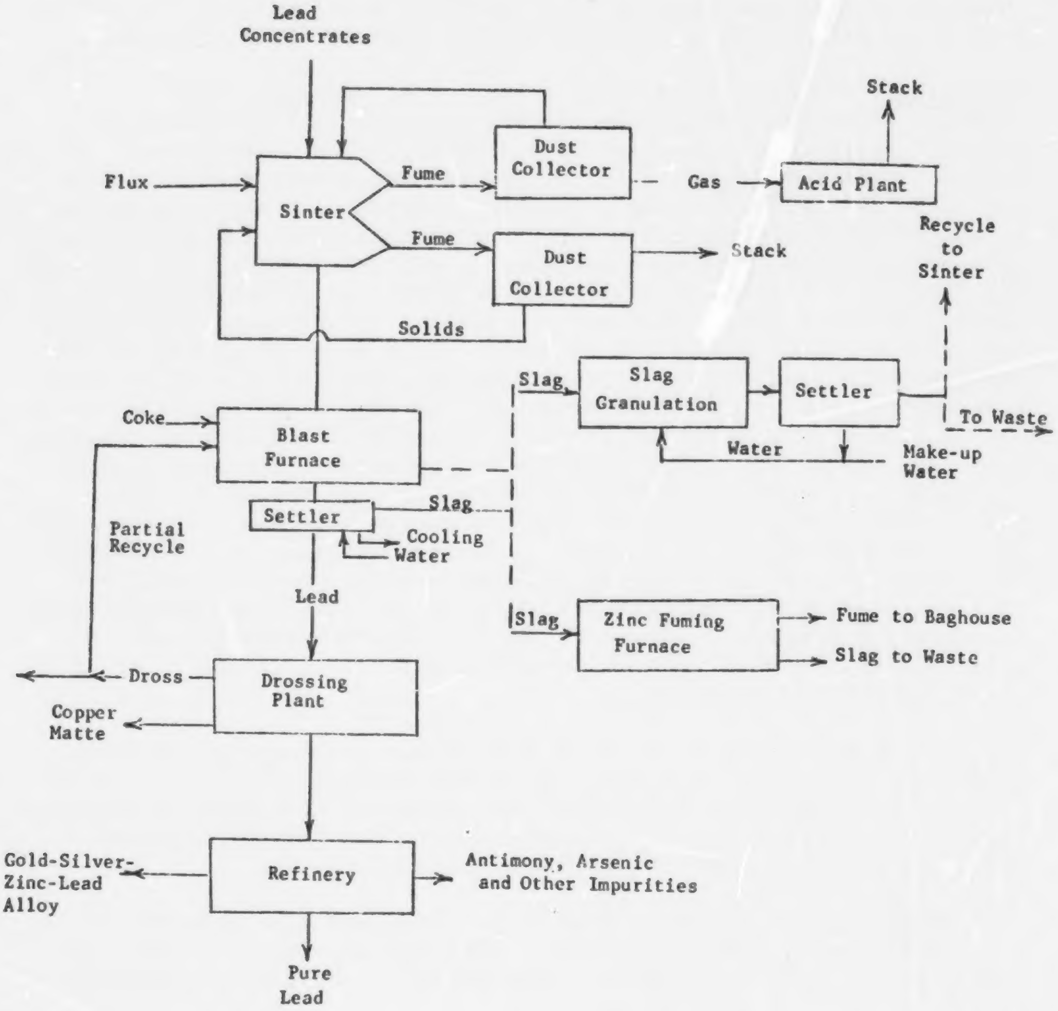


FIGURE 14. GENERALIZED FLOWSHEET OF LEAD SMELTER

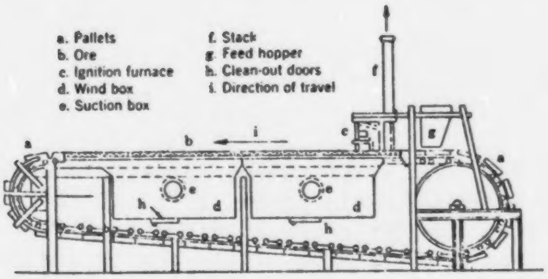
Charge Preparation. General practice in charge preparation (15) may involve the blending of lead concentrates with fluxes and a variety of loose-end products, such as fumes, slags, etc., which contain recoverable lead and other metals. This blended mixture is pelletized after the addition of moisture (up to 10 percent) by rolling in rotating drums or on inclined disks to form spherical pellets about 1/2 inch or more in diameter. The pelletized concentrates are then sintered.

Sintering. Sintering is done on a "sintering machine" which, in essence, is a travelling-grate furnace. Figure 15 illustrates the general structure and function of a downdraft type of sintering machine. The lead industry in the United States uses both this type and also "updraft" sintering procedures, wherein a positive pressure of air is supplied from below the travelling grate of the sintering machine and slightly reduced pressure is maintained above the bed. In the operation, a layer of pelletized concentrates are laid down on the bed of the sintering machine and are ignited by burners above the bed. The balance of the charge (up to about 1 foot deep) is spread on the burning layer, and the travelling grate then enters the windbox section. Under the effect of the applied updraft, the bed burns from the bottom up. The usual United States practice relies on the sintering reaction to remove nearly all sulfur from the concentrates. The sulfur burns off as $SO_2$ in the first portion of the sintering operation. Most plants divide the exhaust gases from sintering into two portions. The gases from the initial portion of sintering contain 4 to 8 percent $SO_2$, are passed through gas-cleaning systems (usually wet scrubbers) and then vented to the atmosphere through a stack. These wet gas scrubbers reportedly operate with closed-circuit scrubbing-water systems, in which the dust- and fume-laden scrubber water is clarified by settling and reused in the scrubbers.

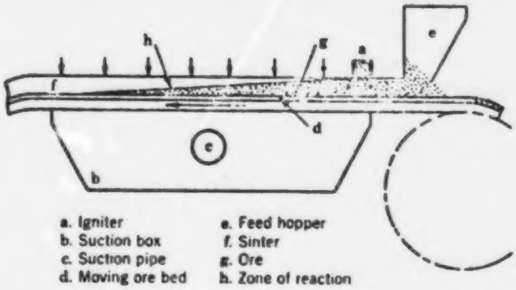
The objectives of the sintering operation are not only to remove sulfur as $SO_2$ and $SO_3$ and to eliminate, by volatilization, much of the undesirable impurities such as arsenic and antimony, but, equally as important, to produce "sinter" of suitable size distribution and strength for subsequent treatment in the blast-furnace process.

The product of the sinter machine is screened and fine material is recirculated to the sintering process. The sinter product is next processed in the lead blast furnace with additions of coke and fluxing agents.

The sintered product fed to the blast furnace will vary in composition from plant to plant. The following tabulation is an example of a finished-sinter composition.



Dwight-Lloyd Sintering Machine



Section Through Dwight-Lloyd Sinter Bed

FIGURE 15. DIAGRAMS OF THE OPERATION OF SINTERING MACHINES(14)

|  | Percent | Oz/Ton |
|---|---|---|
| Cu | 3 | -- |
| Pb | 36 | -- |
| Fe | 10 | -- |
| CaO | 11 | -- |
| Insol | 10 | -- |
| S | 1.4 | -- |
| Zn | 10 | -- |
| Cd | 0.04 | -- |
| Silver | -- | 30-150 |

Blast Furnace Smelting. The lead blast furnace itself is a water-cooled vertical furnace, rectangular in shape, 22 to 28 feet in length and 15 to 20 feet in height, and may range in width from 5 to 10 feet, sometimes being tapered from 10 feet wide at the top to a minimum width of 5 feet. Associated facilities include charging devices, an exhaust-gas-handling system, an air-supply system of bustle pipes and tuyeres for the introduction of air to the charge at several levels, and a refractory-crucible structure at the bottom with provisions for continuous or intermittent tapping of lead bullion and slag. Figure 16 is a diagrammatic sketch of a typical lead blast furnace.

The charge to the blast furnace always includes sinter, coke, and fluxing or slagging additions such as silica and limestone, and generally includes recycled slag from associated operations, cadmium residues, refinery dross, and fume from dust-collecting equipment.

The chemical reactions occurring in the blast-furnace process are complex and numerous:

$$C + O_2 \rightarrow CO_2$$

$$CO_2 + C \rightarrow 2CO$$

$$PbO + CO \rightarrow Pb + CO_2$$

$$Cu_2O + CO \rightarrow 2Cu + CO_2$$

$$Sb_2O_3 + 3CO \rightarrow 2Sb + 3CO_2$$

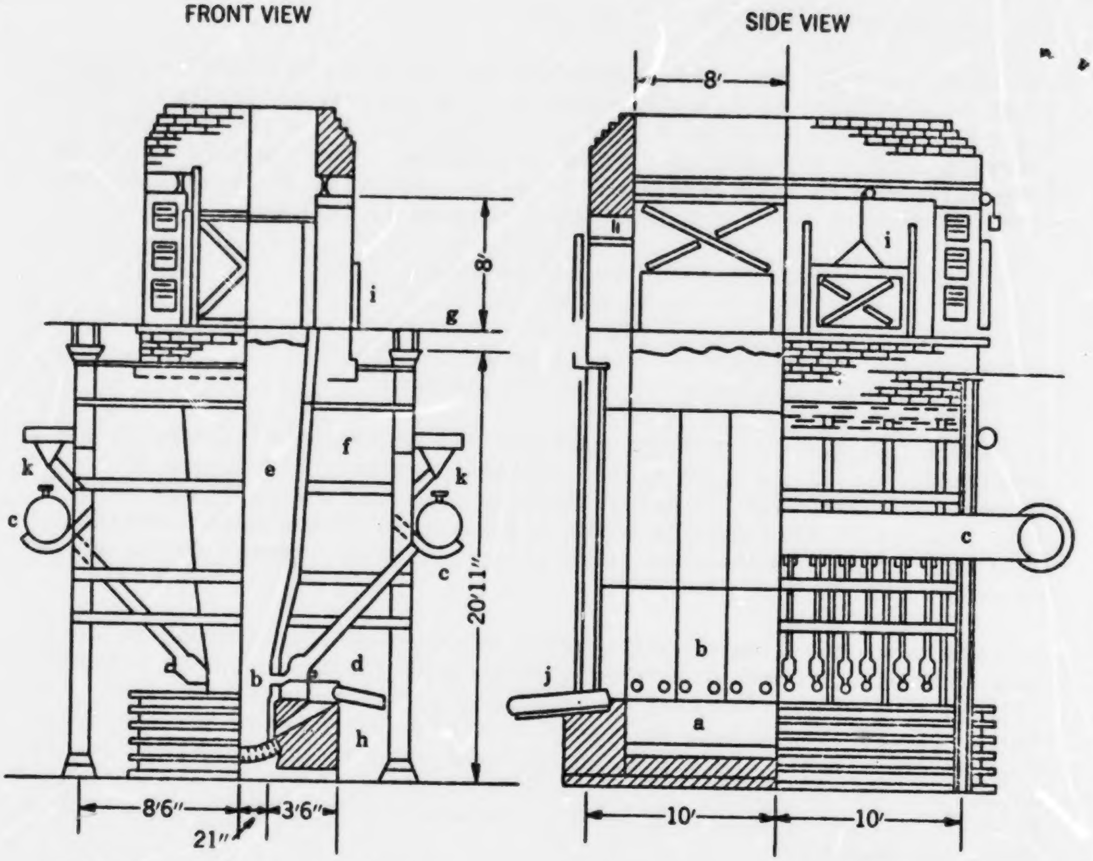
$$As_2O_3 + 3CO \rightarrow 2As + 3CO_2$$

$$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2$$

$$Fe_3O_4 + CO \rightarrow 3FeO + CO_2$$

$$FeO + CO \rightarrow Fe + CO_2$$

$$PbS + Fe \rightarrow Pb + FeS$$



a. Hearth or crucible
b. Tuyeres
c. Bustle pipe
d. Lead well
e. Shaft
f. Water jackets
g. Charge floor
h. Arents siphon tap
i. Charge doors
j. Slag spout
k. Relief valve

FIGURE 16. DIAGRAMMATIC SKETCH OF A TYPICAL LEAD BLAST FURNACE(14)

$$PbO + Fe \quad Pb + FeO$$

$$2PbO + PbS \quad 3Pb + SO_2$$

$$PbSO_4 + PbS \quad 2Pb + 2SO_2.$$

The products of the blast furnace are:

(a) Base bullion (18), which normally may contain quantities of copper, arsenic, antimony, or bismuth, which must be removed by further processing to produce an acceptable lead. The lead bullion also may contain precious metals in quantities worth recovering. The composition of the base bullion will vary from plant to plant, but will in general contain 95 to 99 percent lead with impurities ranging as follows:

Copper -- up to 2.5 percent
Zinc -- negligible
Antimony -- up to 2 percent
Arsenic -- up to 1 percent
Bismuth -- up to 0.03 percent.

(b) Slag, consisting of iron, calcium, and magnesium silicates, substantially all of the zinc in the original charge (up to about 15 to 20 percent zinc), small quantities of arsenic and antimony, and variable amounts of lead (1.5 to about 4 percent). If the slag contains more than about 6 percent of zinc, it is generally treated for zinc recovery.

In this case, the slag, usually while still molten, is charged to a zinc fuming furnace, commonly a reverberatory-type furnace, with or without additions of other zinc-bearing materials (other recycled drosses, dusts, etc.). The charge is heated to a high temperature through addition of fuel (coal) and air blown into the molten slag, and the zinc is boiled off and oxidized to zinc oxide dust particles which are collected in dust-collecting equipment such as cyclones, precipitators, dust chambers, and baghouses.

Lead blast-furnace slags also may be granulated by impacting a stream of molten slag with a high-pressure water jet. The granulated slag may be dewatered and either recycled as part of the charge materials to the sinter process, or, depending on slag composition and plant facilities, may be totally discarded.

The slag-granulating water circuit is usually closed to allow recovery of the slag in settling tanks with the clarified water recirculated. Water loss by evaporation during granulating may be made up with waste water from other plant operations such as cooling-tower blowdown or neutralized effluent from an associated acid plant.

(c) Matte. In some blast-furnace practice, a matte phase consisting of copper and iron sulfides may be formed as a discrete liquid layer between bullion and slag and may be isolated. This material is usually sent to copper smelters for further treatment.

Refining Operations. Impure base bullion, containing copper, antimony, arsenic, precious metals, and bismuth, requires additional refining. After production of the base bullion (18) the preliminary refining steps, drossing (19) and softening (20), are always carried out in sequence. Thereafter, two routes to refined lead are available: fire refining (21) and electrolytic refining (22). These operations are discussed in the following sections. The descriptions given here are subject to the variations of individual plant practice.

Drossing (19). Drossing is performed in vessels referred to as kettles. The kettles are generally hemispherical in shape, up to 24 feet in diameter, and are constructed of welded steel plate up to 1-1/2 inches thick, holding up to 250 tons. The kettles are gas heated with external refractory-brick insulation. Permanent auxiliary equipment for stirring, skimming, transfer of products, etc., is generally provided. The major purpose of drossing is to remove copper. The separation of copper is effected by lowering the temperature of the metal close to, but slightly above, the melting point of lead. At this temperature the solubility of copper in lead is minimal and excess copper is rejected from the melt to form a crust or head on the melt. This is separated by skimming from the liquid lead. In some practice, sulfur is added to the drossing kettle to enhance the removal of copper as copper sulfide, which also appears in the crust. By drossing, the copper content of the lead is reduced from as high as several tenths of a percent to as low as 0.005 percent. The liquid lead is then transferred to a second kettle, where a second decoppering cycle may be performed. The dross, which may typically contain about 90 percent lead oxide, 2 percent copper, and 2 percent antimony, with entrained gold and silver, is re-treated in a by-product reverberatory furnace to recover lead as bullion and to produce a copper matte for subsequent treatment by copper smelter practice.

Softening (20). After drossing to remove the major portion of copper, the bullion is then subjected to a "softening" operation for removing antimony, arsenic, and tin. The term "softening" is used because the removal of the impurities, principally antimony, produces a product of lower hardness and strength. In contrast, lead alloyed with antimony is commonly referred to as "hard lead" or antimonial lead.

The softening may be done in either of two ways, either by air oxidation of the molten bullion in a reverberatory furnace or by oxidative slagging with a flux of sodium hydroxide and sodium nitrate.

The air-oxidation process consists of treatment of drossed lead in a reverberatory-type furnace with air introduced into the bath through pipes or lances. In the air-oxidation method of softening, most of the impurities are removed in a primary slag which is skimmed off. The aeration is continued with the formation of a final slag. This two-stage slagging permits the maximum degree of removal of impurities. The slag produced contains the oxides of copper, arsenic, antimony, and tin as complex oxides (lead stannate, lead arsenate, lead antimonate) and entrained metal, and is further treated to recover antimony, antimony oxide, antimonial (hard) lead, a tin-rich skim (sold to tin-recovery operations), and sodium arsenate, which is generally discarded.

After softening by the air-oxidation, reverberatory-furnace treatment, the lead bullion is drained from beneath the slag and treated by fire or electrolytic refining.

An alternative method of softening is an oxidative slagging technique in which a sodium hydroxide-sodium nitrate mixture is stirred into the molten lead to oxidize arsenic, antimony, tin, etc., which enter the slag as arsenates, antimonates, and stannates of sodium. At least two versions of the oxidative slagging process are used, the kettle process and the Harris process. The major difference between them is that, in the kettle process, the resulting slag is discarded to waste, while in the Harris process the slag is extensively treated by a hydrometallurgical process to recover sodium hydroxide and, where indicated, arsenic, antimony, and tin products.

Figure 17 illustrates the various modifications of the softening step.

Fire Refining (12). The fire refining of lead has as its objective the removal of silver, gold, and bismuth, the bulk of which metals are not removed in drossing and softening. Figure 18 illustrates the fire refining process. It is comprised of the following steps:

(1) Desilvering by the so-called Parke's process in which the softened lead is treated with zinc metal at about 900 F, with stirring, for several hours. The zinc combines preferentially with gold and silver to form zinc-gold and zinc-silver compounds which are virtually insoluble in lead and which are lighter than lead. Enough zinc is added to combine with all the gold and silver and to saturate the lead with zinc. The zinc-precious metal alloys accumulate on the surface and are skimmed off. By conducting the desilvering in two stages as is indicated in Figure 18, it is possible to isolate high-gold and high-silver products to facilitate the recovery of these metals in subsequent processing.

(2) After removal of the gold and silver, zinc is removed by a process called vacuum dezincing, conducted in a separate kettle, using a portable bell-shaped vessel whose open bottom is lowered into the liquid lead to form a seal and allow evacuation of the space above the melt. The upper portion of the dezincing chamber contains a condenser, a stirrer which extends down into the melt, and connections to the vacuum system. As vacuum is applied to the chamber, any zinc in the lead leaves the melt by vaporization and condenses on the condenser.

Electrolytic Refining (24). Electrolytic refining of lead utilizes anodes cast from partially refined or softened lead. The process

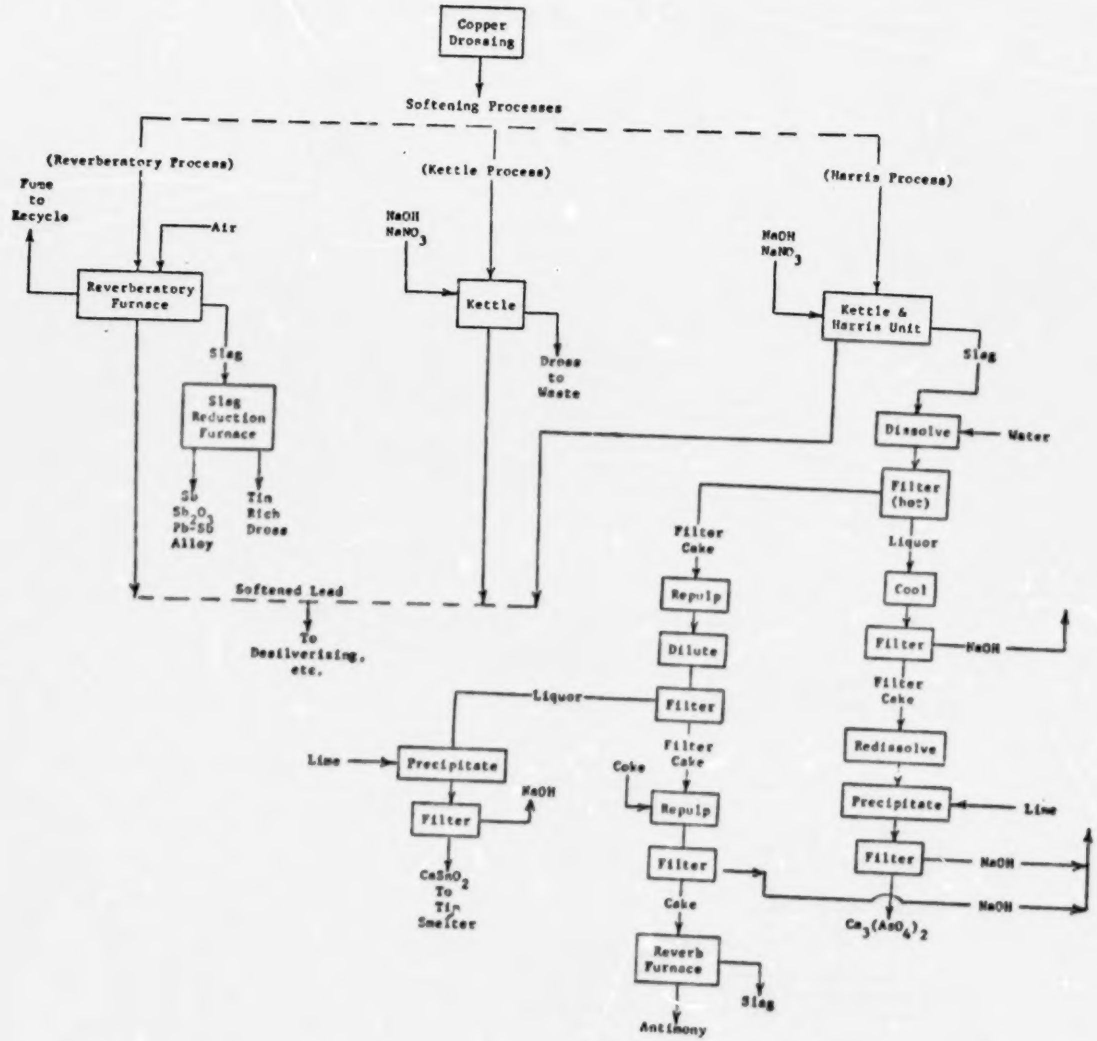


FIGURE 17. DIAGRAM OF ALTERNATIVE LEAD-SOFTENING PROCEDURES(13,15)

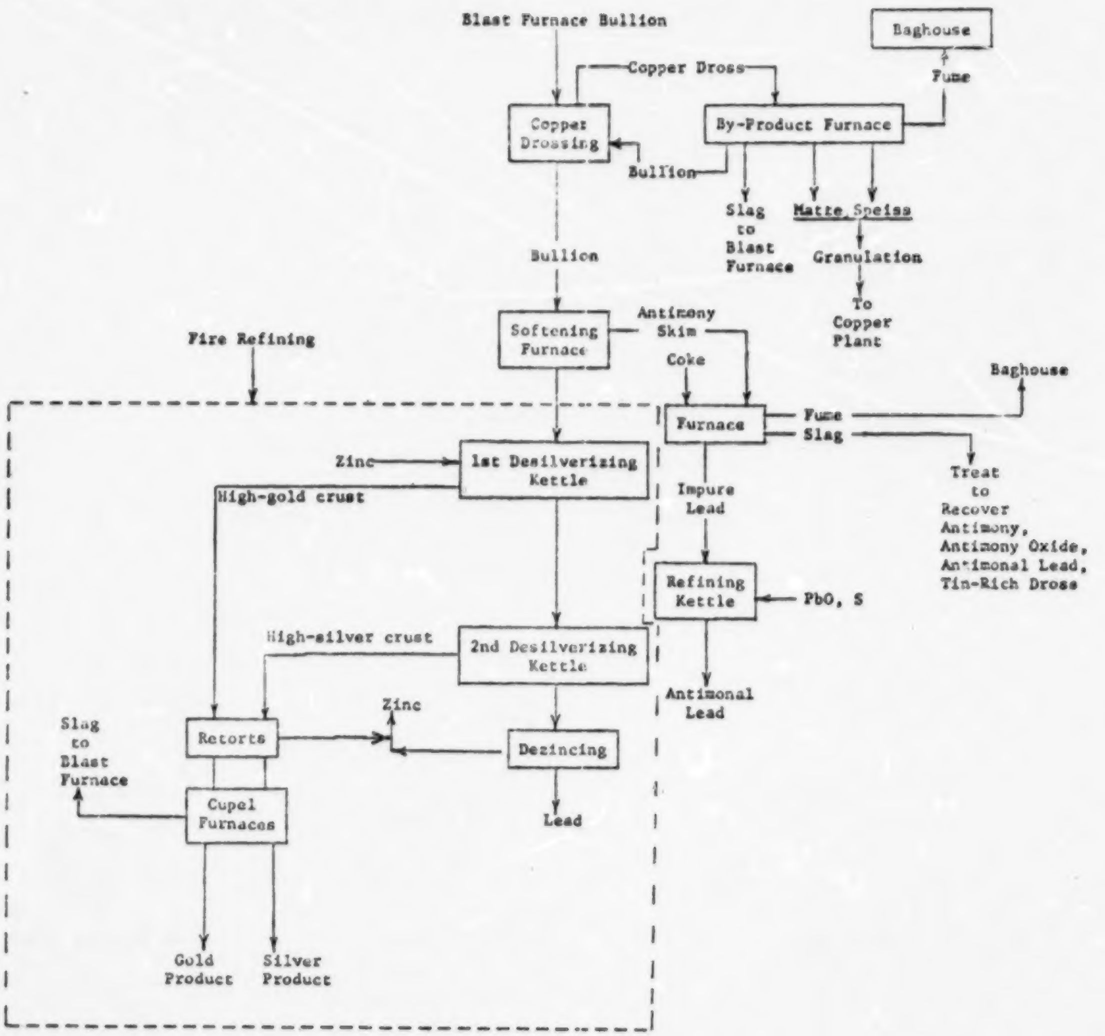


FIGURE 18. DIAGRAM OF STEPS IN FIRE REFINING OF LEAD(13,15)

involves the transfer of lead from the impure anode through a hydrofluosilicic acid electrolyte and deposition on the cathode, consisting of a starting sheet of electrolytically refined lead. Impurities or contained metal values determine the feasibility of electrolytic refining. The by-products include bismuth, gold, silver, selenium, tellurium, antimony, and arsenic.

Formerly, the electrolytic process was the only feasible method for producing refined lead with an extremely low bismuth content. In late years, a fire-refining technique for debismuthizing lead has provided some competition for the electrolytic process in this respect.

The cast anodes are suspended in cells alternating with starting sheets with approximately 2 inches between electrodes. Anodes weighing about 400 pounds and approximately 3 feet long by 2 feet wide are suspended alternately between starting sheets in wood or concrete tanks lined with asphalt. A typical cell is about 2-1/2 feet wide by 4 feet deep and 8 feet long. The cells are arranged in banks as in copper electrolysis (see section on copper). Except for the nature of the metal, the electrolyte, and electrical conditions, the operation is similar to copper refining.

The electrolyte used in lead refining is fluosilicic acid, $H_2SiF_6$, and is usually operated at temperatures of about 100 F. This acid is highly corrosive and thus rubber or plastic piping is used for its circulation. The electrolyte is prepared in the plant by the reaction of sulfuric acid with fluorspar to produce hydrofluoric acid which reacts with silica to form hydrofluosilicic acid

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF$$

$$6HF + SiO_2 \rightarrow H_2SiF_6 + 2H_2O.$$

The active compound in the electrolysis is identified as lead fluosilicate, which forms when the lead reacts with fluosilicic acid:

$$2H_2SiF_6 + 2Pb + O_2 \rightarrow 2PbSiF_6 + 2H_2O.$$

In operation, the cast anodes and starting sheets are placed in the tanks and electrolysis is carried out for about 4 days, after which all electrodes are removed from the cell and washed. The cathodes, refined lead, are melted and cast into product forms. The anodes are washed to recover electrolyte adhering to their corroded surfaces and to remove slimes, and then returned to the electrolytic cell for production of a second cathode. Each anode of about 400 pounds will yield two refined-lead cathodes weighing about 180 pounds each.

The slimes of residual impurities which separate during the electrolysis contain arsenic, antimony, gold, bismuth, silver, etc. The slimes are dewatered by centrifuging or filtering and the solid residues are treated for the recovery of valuable materials. Slimes treatment is described in other sections of this discussion.

## Refined Lead (22,25)

Refined lead produced by fire refining or electrolytic refining is melted and cast into pigs. Various grades, based on specifications, are produced. These are shown in Table 23.

TABLE 23. CHEMICAL SPECIFICATIONS FOR COMMERCIAL PIG LEAD(16)

| | Corroding lead [1] | Chemical lead [2] | Acid lead [3] | Copper lead [4] | Common desilverized lead A [5] | Common desilverized lead B [5] | Soft undesilverized lead [6] |
|---|---|---|---|---|---|---|---|
| Silver..........maximum percent.. | 0.0015 | 0.020 | 0.002 | 0.020 | 0.002 | 0.002 | 0.002 |
| Silver..........minimum percent.. | -------- | .002 | -------- | -------- | -------- | -------- | -------- |
| Copper..........maximum percent.. | .0015 | .080 | .080 | .080 | .0025 | .0025 | .04 |
| Copper..........minimum percent.. | -------- | .040 | .040 | .040 | -------- | -------- | -------- |
| Silver and copper together maximum percent.. | .0025 | -------- | -------- | -------- | -------- | -------- | -------- |
| Arsenic..........maximum percent.. | .0015 | -------- | -------- | -------- | -------- | -------- | -------- |
| Antimony and tin together maximum percent.. | .0095 | -------- | -------- | -------- | -------- | -------- | -------- |
| Arsenic, antimony and tin together maximum percent.. | -------- | .002 | .002 | .015 | .015 | .015 | .015 |
| Zinc..........maximum percent.. | .0015 | .001 | .001 | .002 | .002 | .002 | .002 |
| Iron..........maximum percent.. | .002 | .002 | .002 | .002 | .002 | .002 | .002 |
| Bismuth..........maximum percent.. | .05 | .005 | .025 | .10 | .15 | .25 | .005 |
| Lead (by difference)......minimum percent. | 99.94 | 99.90 | 99.90 | 99.85 | 99.85 | 99.73 | 99.93 |

[1] Corroding lead is a designation that has been used for many years in the trade to describe lead which has been refined to a high degree of purity.

[2] Chemical lead has been used for many years in the trade to describe the undesilverized lead produced from southeastern Missouri ores.

[3] Acid lead is made by adding copper to fully refined lead.

[4] Copper lead is made by adding copper to fully refined lead.

[5] Common desilverized leads A and B are designations that are used to describe fully refined desilverized lead.

[6] Soft undesilverized lead is used in the trade to describe the type of lead produced from ores of the Joplin, Mo., district.

## Zinc Production

## Zinc Concentrates (9)

Zinc concentrates produced by flotation are variable in grade, depending on the complexity and type of the ore. Data gathered about 10 years ago indicated that zinc concentrates from the milling of zinc and lead-zinc ores averaged about 59 percent zinc, and concentrates from copper-lead-zinc ores averaged about 53 percent zinc.

## Roasting (25)

There are two general routes to the production of refined zinc, the pyrometallurgical and the hydrometallurgical, involving leaching and electrolysis. Sulfur removal is always required, regardless of the path followed.

The purpose of roasting zinc concentrates is to eliminate most of the sulfur in sphalerite and to convert zinc sulfide to zinc oxide or zinc sulfate. When the pyrometallurgical route is to be followed, as complete removal of sulfur as possible is advantageous. If the hydrometallurgical route is followed, the objective of roasting is to convert the acid-insoluble sphalerite to acid-soluble zinc oxide with controlled amounts of zinc sulfate, and to avoid the formation of zinc ferrite. The main reactions occurring in roasting are:

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

$$2ZnO + 2SO_3 \rightarrow 2ZnSO_4.$$

These reactions are controlled to produce the desired amount and form of residual sulfur, depending on whether the roasted product is intended for pyrometallurgical reduction or for electrolytic reduction to metal.

Currently used methods of roasting are

(1) Multiple-hearth furnace roasting

(2) Flash roasting

(3) Fluidized-bed roasting.

In multiple-hearth furnace roasting, the concentrates are fed through a large cylindrical furnace with a number (up to 12) of circular hearths one above another. Rotating arms with attached rakes move the charge of concentrates inward and outward on alternate hearths so that the charge falls (through ports) from one hearth to the next, countercurrent to a stream of hot gases. The roasted calcine product is discharged at the bottom of the furnace. Oxidation of the charge supplies some heat to support the process, but additional fuel in the form of coal, oil, or gas is usually supplied. Temperature control to avoid the formation of ferrites and regulate the amount of zinc sulfate is achieved by introducing cooling air at certain hearth stages.

In flash roasting, the concentrates are showered into a stream of hot gases in large cylindrical furnaces. As the concentrates descend, oxidation is extremely rapid, much more so than in the multiple-hearth furnace chamber.

In fluidized-bed roasting, the concentrates are kept in agitated suspension by a stream of upward-flowing combustion gases. The suspended particles form a "fluid" bed, virtually homogeneous with respect to temperature and composition. Concentrates are fed to fluidized-bed roasters either dry or in slurry form; fluidizing air and combustion gas is supplied from a blower to a windbox below the bed. The fluidizing gas is distributed by means of a perforated plate or a multitude of small pipes at the bottom of the bed to ensure constant upward velocity through the cross section of the bed. As feeding of concentrates progresses, the bed overflows through a discharge port. Fluidized-bed roasters may be up to 20 feet in diameter. Bed depths will range to 6 feet deep when in a fluidized condition. Capacities up to 10 tons per hour have been obtained with equipment of this size.

One of the major advantages of fluidized-bed roasting is the excellent control of temperature it affords. This is important in the avoidance of ferrite formation and the regulation of the sulfur content of the roasted product.

Equipment auxiliary to roasting operations is (in the usual operating sequence): waste-heat boilers, dust-catching equipment (usually cyclones), electrostatic precipitators, gas-cooling and/or -cleaning towers, and sulfuric acid plants. Gases produced in the roasting of zinc concentrates contain from about 9 to 13 percent $SO_2$ and these are sent to sulfuric acid plants.

## Sintering (26)

Another method of oxidizing the sulfur from zinc concentrates is by the Dwight-Lloyd sintering process. The sintering machine has been described previously in this section (Figure 15, page 93). In zinc metallurgy, unlike lead metallurgy, sintering is done almost exclusively by downdraft methods. Roasted or raw sulfide concentrates, mixed with other charge components (e.g., coal, silica sand, lime), are deposited on the first portion of the bed through hoppers or nozzles. The charge is carried on the travelling grate beneath burners which serve to ignite the upper surface of the bed, and then over a windbox which serves to draw air and combustion gases down through the burning sinter bed. After the sintering reaction, the sinter product falls from the end of the returning sinter plates and is sized for use in the following reduction operations. In the sintering of zinc concentrates, which are apt to contain cadmium, chlorides in some form (either salt or chloride solutions from cadmium recovery operations) may be intermixed with the sinter feed. These chlorides assist in the volatilization and removal of lead, cadmium, and silver during sintering.

Sintering accomplishes the aim of agglomerating the zinc-bearing materials in a product whose size and strength are suitable for the pyrometallurgical furnacing process. In most plants, a selected part of the sinter product is recirculated to assure proper removal of lead, cadmium, and sulfur, and to achieve the desired degree of densification.

## Retorting (27) and Condensation (28)

Retorting is a reduction-volatilization process in which zinc oxide, produced by roasting and briquetting, by roasting and sintering, or by sintering alone, is reacted with coal or coke at high temperature.

The reactions which occur during retorting are:

$$ZnO + C \rightarrow Zn + CO$$

$$2ZnO + C \rightarrow 2Zn + CO_2$$

$$ZnO + CO \rightarrow Zn + CO_2$$

$$CO_2 + C \rightarrow 2CO$$

$$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$$

$$Fe_2O_3 + C \rightarrow 2FeO + CO$$

$$ZnS + Fe \rightarrow Zn + FeS$$

$$Zn + CO_2 \rightarrow ZnO + CO \text{ (blue powder formation)}$$

$$Zn_2SiO_4 + 2C \rightarrow 2Zn + 2CO + SiO_2$$

$$FeO + SiO_2 \rightarrow xFeO \cdot SiO_2 \text{ (slag formation).}$$

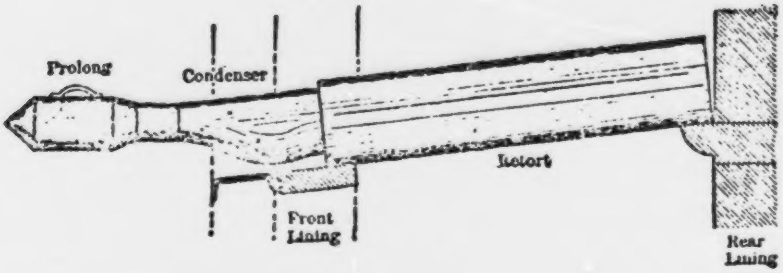
At the temperature of retorting (about 1200 C), the reduced zinc is vaporized and carried out of the retort with carbon monoxide to condensing systems. Three methods of retorting are used in the United States. They are:

(1) The batch horizontal retorting process

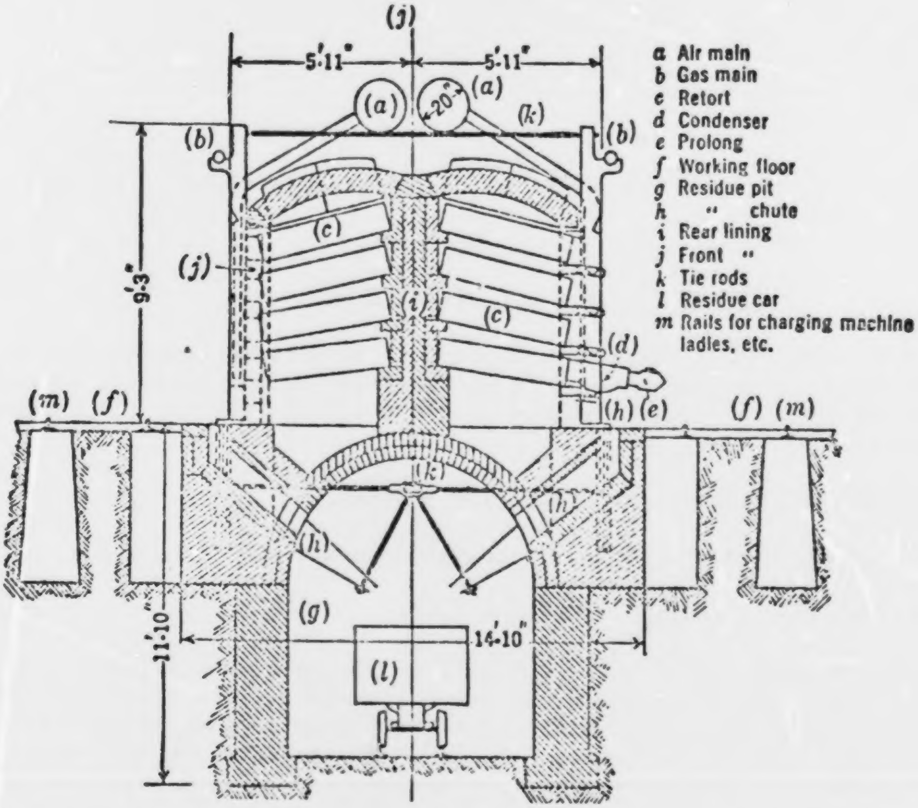
(2) The continuous vertical retorting process

(3) The electrothermal retorting process.

The horizontal-retort plant consists of a long narrow furnace into which fire-clay retorts are inserted crosswise to the length of the furnace as shown in Figure 19. Up to 600 retorts are arranged in banks on either side of the heating chamber. The retorts are cylinders up to 9.5 inches in diameter and about 5 feet in length with wall thicknesses of about 1 inch. They are made of carefully selected mixtures of refractory clays. The butt end of each retort is closed. The open outer end is "luted" or sealed by fireclay packing to a refractory condenser which collects the evolved zinc vapor until it is removed. Metal extensions to the condensers, called prolongs, may be used to collect vapor that escapes the condensers.



Retort for zinc distillation as set in furnace with condenser and prolong



Horizontal distillation furnace

FIGURE 19. ILLUSTRATIONS OF THE ELEMENTS OF THE HORIZONTAL RETORT OPERATION(17)

The charge to the retorts varies from plant to plant, but as an example, the charge at one plant consists of roughly 57 percent sinter, 22 percent zinc oxide, 19 percent coal and coke, and small amounts of dross, salt, and fluorspar. Charging is done mechanically. The retorts are heated in a controlled cycle to a maximum charge temperature of about 1200 C and then allowed to cool before emptying and recharging. The cycle from charge-to-charge may take 1 to 2 days. Zinc metal, called spelter, is periodically removed from the condensers during the cycle. The spelter, in addition to zinc metal, may contain some lead, and most of the cadmium in the charge. Part of the lead is removed later in refining. During retorting, some of the zinc is superficially oxidized by $CO_2$ (reaction 8 above) in the condenser, does not coalesce to enter the liquid phase, and is collected as a dust called blue powder. This is recirculated to retorting.

Recovery of zinc in horizontal retorting may exceed 90 percent. After retorting is finished, the residues, amounting to about 25 percent of the weight of the original charge, and containing from 5 to 15 percent zinc, are removed. If the residue is sufficiently rich in lead, gold, and silver, it is usually shipped to a lead smelter for recovery of these values.

The continuous vertical-retort reduction process is carried out in a large (roughly 1 by 5 by 25 feet high) retort constructed of silicon carbide within a combustion chamber, with a refractory-brick outer covering, heated by suitably positioned gas burners. The charge to the furnace consists of briquettes containing a compacted mixture of anthracite coal and zinc calcine. The briquettes are prepared by mixing finely ground coal and calcine with a tar or similar binder, compressing the mixture into small pillow-shaped forms, and heating these forms in a furnace to a temperature of about 900 C. The heat-treatment operation hardens the briquettes and removes volatile materials.

The prepared briquettes are charged at the top of the vertical-retort furnace through a movable-lid arrangement. As the charge progresses downward through the retort, the reduction reaction proceeds, liberating zinc vapor and carbon monoxide. The zinc vapor is led from the upper portion of the retort through a refractory passage to impinge upon and condense in an agitated pool of molten zinc. The furnace gas (largely CO) is drawn through the condensing chamber into a gas scrubber and recycled to the burners. The liquid zinc product is transferred to holding furnaces or distilling columns. Recovery of zinc in vertical-retort furnaces exceeds 90 percent, and blue-powder production amounts to only about 3 percent of the zinc charged, considerably less than in horizontal batch retorting. The residue also contains considerably less zinc than that from batch retorts.

The electrothermic process of the St. Joe Minerals Corporation utilizes a relatively hard, strong sinter and coke as the charge to the top of the furnace, which is roughly 8 feet in diameter and 30 to 40 feet in height. The power input to the furnace consists of electrical power supplied through three pairs (upper and lower) of electrodes which results in a flow of electrical current directly through the charge, producing a resistance-heating effect. The vaporized zinc is collected by means of an annular ring at about mid-height on the furnace. The zinc vapor is drawn into a U-shaped condenser filled with molten zinc. The exit side of the U-shaped tube condenser is connected through a gas washer to a vacuum system. The furnace gas is essentially carbon monoxide which is used as a fuel gas for other plant operations. The zinc metal is continuously bled from the condenser and led to purifying distillation columns.

Figure 20 illustrates the electrothermic retorting equipment.

Auxiliary operations for recovering zinc from miscellaneous materials such as zinc-bearing lead blast-furnace slags and low-grade materials (as concentrator tailings, retort residues, plant sweepings, etc.) include slag fuming and Waelz furnacing.

## Refining (29)

Some portion of the output of a zinc smelting furnace may require subsequent refining depending on such factors as the current market for various grades of zinc, the concentrates used, the quantities of metals other than zinc (cadmium, lead, gold, silver, etc.) present in the spelter, or the conditions of the particular smelting process. Refining may be accomplished by any of three methods: liquation (30), distillation (31), or electrolysis (34). Electrolysis is discussed later.

Liquation. Liquation is the term used to denote a process of separating impurities on the principle of liquid solubilities and freezing points. In the liquation process, impure molten zinc is cooled to a temperature just above its freezing point. As the temperature is decreased, the solubilities of lead and iron in the zinc decrease. As the zinc cools, the lead and iron are, to a major degree, rejected from the liquid zinc. The lead and iron rejected constitute intermediate products, which may be further treated for the recovery of the metals or may be transferred or sold to another plant. The purified zinc is cast into salable form.

Distillation (31). Distillation also is used to purify the spelter zinc and to separate and recover lead and cadmium as by-products. Distillation is carried out in vertical fractionating columns. These columns are constructed of silicon carbide and enclosed in gas-fired heating chambers. The impure spelter zinc, containing lead and cadmium, is fed into the top of the first distillation column, which is maintained at a temperature below the boiling point of lead but above the boiling point of zinc and cadmium. Lead containing small amounts of zinc and cadmium is drawn from the bottom of the first column. Most of the zinc and cadmium vaporizes and passes from the first column through a heated

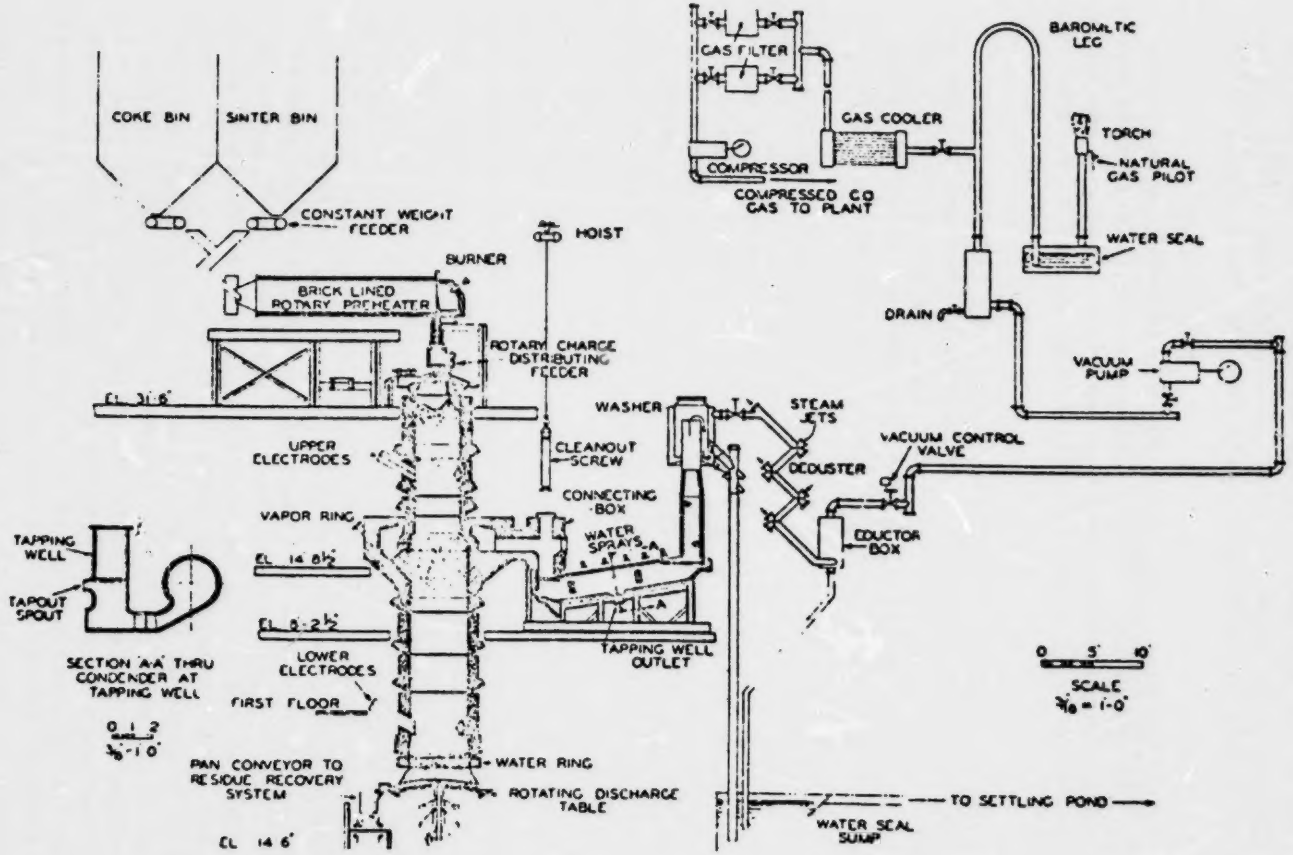


FIGURE 20. SCHEMATIC DRAWING OF THE ELECTROTHERMIC ZINC REDUCTION FURNACE(17)

and insulated carryover to a second column which is maintained at a temperature below the boiling point of zinc and above the boiling point of cadmium. The zinc condenses as a pure liquid and is discharged from the bottom of the second column to casting or alloying operations. The cadmium fraction in the overhead from the second column and the impure lead-zinc-cadmium bottoms from the first column are treated for the recovery of these metals as described in the section dealing with primary cadmium.

Electrolytic Refining (32 through 35). The electrolytic process possesses several advantages over fire-refining methods. It is applicable to low-grade concentrate. Impurities are readily removed and can be recovered as valuable products, and zinc of as high purity as desired can be made.

In the electrolytic reduction of zinc to metal, the calcines are leached to dissolve the soluble salts of zinc and other metals, the solution is purified, and pure zinc is plated from the leach liquid. The spent electrolyte, after electrolysis of the zinc, is returned to the leaching step. An example of process steps is presented in Figure 21.

The process steps involve first the leaching of the calcine with dilute sulfuric acid. Leaching may be done continuously or by batch. If batch leaching is done, tankage capacity in the leaching section must be about doubled to compensate for time lost in filling and emptying tanks. Continuous leaching has the disadvantage of requiring a feed of uniform composition with respect to impurities and, for this reason, batch leaching is more widely employed; leaching is generally done in Pachuca tanks (Figure 22).

Two general types of leaching, single and double, are employed.

In single leaching, the calcines are treated with spent electrolyte until all of the zinc is dissolved in a still-slightly-acid medium. Lime is then added to precipitate all of the iron, silica, antimony, and arsenic present. Extremely good control is required to avoid the loss of significant quantities of zinc by coprecipitation. Double leaching avoids the necessity for such control. In double leaching, the calcines are leached with a deficit of spent electrolyte so that the resulting solution is safely on the basic side, and impurities such as iron, arsenic, etc., remain undissolved. Clarified leach liquor from this first stage is sent to the purification step. The residue, still containing some zinc, is separated and sent to a second stage of leaching where it is treated with a slight excess of acid in spent electrolyte. The resulting acidic solution is then combined with additional spent electrolyte and recirculated to the first stage of leaching. In either case, the leach liquor is clarified in thickeners and filtered. The filter cake is generally shipped to a lead smelter for the recovery of lead and precious metals which do not dissolve in leaching. The filtered solution is treated with zinc dust in the so-called purification step (33) to precipitate cadmium, copper, nickel, and cobalt and

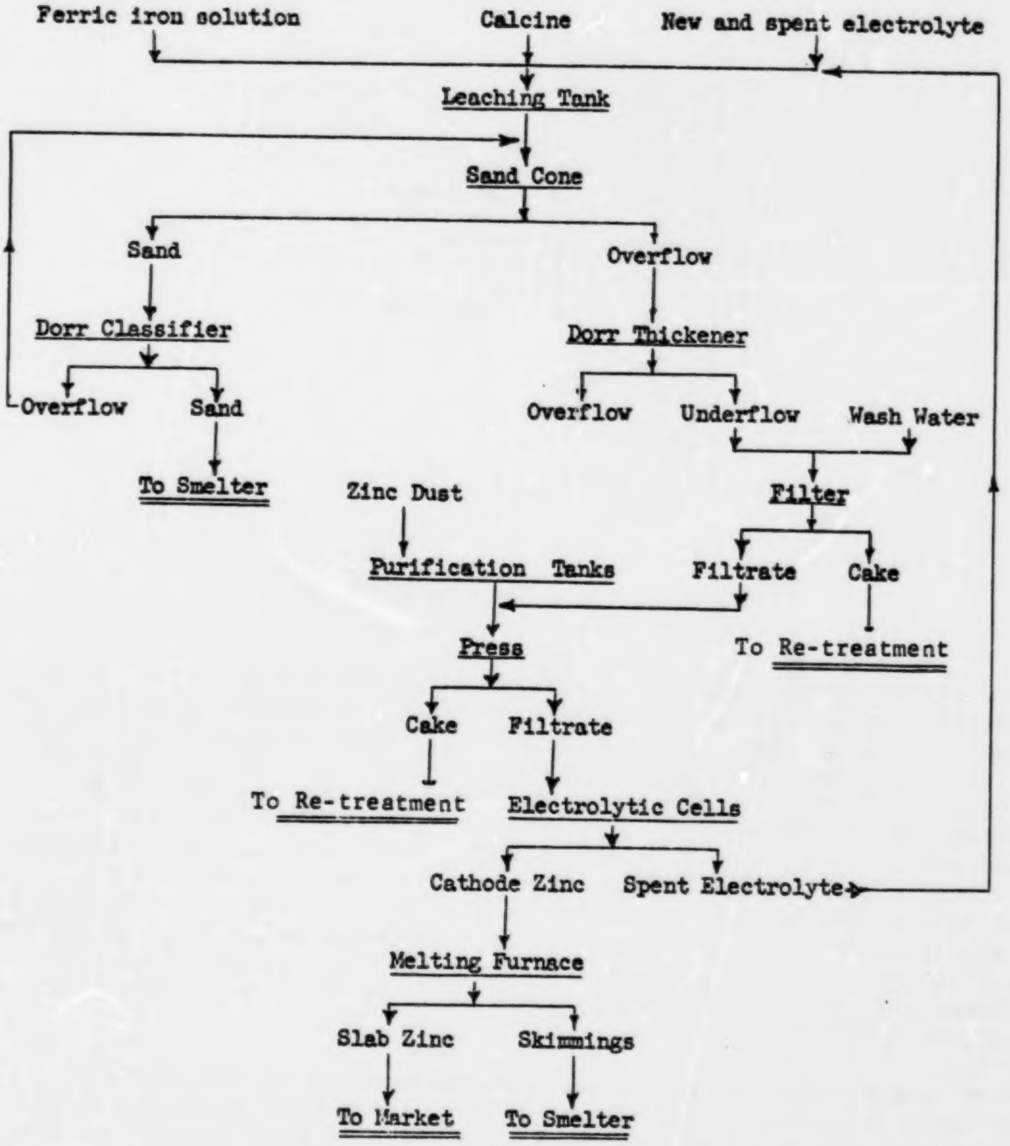


FIGURE 21. TYPICAL FLOWSHEET OF AN ELECTROLYTIC ZINC PLANT(17)

refiltered. This filter cake may be treated to reclaim cadmium or other metals. The filtrate may be re-treated the same way to reduce the impurities to even lower levels. The purified solution is sent to the electrolytic cells (34).

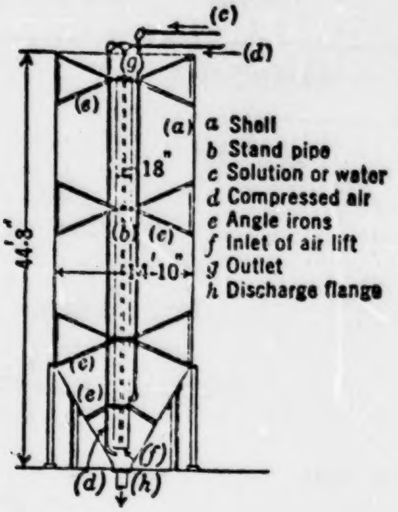


FIGURE 22. THE PACHUCA TANK(17)

The electrolytic deposition of the zinc from the purified zinc sulfate solution follows generally the process described previously in this report for the electrowinning of copper. Insoluble anodes (lead alloyed with about 1 percent silver) and aluminum starting-sheet cathodes are the electrodes used. The anodes are 2-1/2 x 4 feet and are 3/8-inch thick. The aluminum starting sheets are approximately the same length and width and are about 3/16-inch thick. Tanks are usually constructed of concrete with lead linings. Zinc electrowinning operations are classified by the current density used in the cell and the acid concentration, with the lower ranges of the combination being 20 to 40 amperes per square foot and 6 percent acid strength. High ranges of the two parameters are 100 amperes per square foot and 25 to 30 percent $H_2SO_4$ acid concentrations.

The zinc deposited on the aluminum starting sheets is periodically stripped to obtain a slab of zinc metal. These anode slabs are subsequently melted and cast into commercial forms of slabs or pigs to form the product of the primary zinc industry. The melting operation may include the addition of, for example, 3-1/2 percent aluminum to the pure zinc to produce pigs or slabs of alloyed zinc for later remelting in zinc-die-casting shops.

# SECTION IX

## THE CADMIUM INDUSTRY

### Size and Characteristics

There is no discrete primary cadmium industry. Primary cadmium metal and compounds are by-product materials produced by companies principally engaged in the recovery of zinc either as a major value or as a by-product itself. This is because there is no separate ore of cadmium and because it occurs in significant quantities in nature exclusively in association with zinc sulfides. Major cadmium producers in the United States are shown in Table 24.(1)

TABLE 24. PRODUCERS OF CADMIUM METAL(1)

| | |
|---|---|
| American Smelting and Refining Co. | Denver, Colorado<br>Corpus Christi, Texas |
| American Zinc Co. | East St. Louis, Illinois |
| The Anaconda Co. | Great Falls, Montana |
| Blackwell Zinc Co. | Blackwell, Oklahoma |
| The Bunker Hill Co. | Kellogg, Idaho |
| Eagle Picher Inds. Inc. | Galena, Kansas |
| National Zinc Co. | Bartlesville, Oklahoma |
| The New Jersey Zinc Co. | Palmerton, Pennsylvania |
| St. Joe Minerals Corp. | Monaca, Pennsylvania |
| United Refining and Smelting Co. | Franklin Park, Illinois |

In 1969, the production of cadmium from various sources was distributed as follows(1):

| Source | Pounds |
|---|---|
| Zinc recovery operations | |
| Furnacing | 6,800,000 |
| Electrolytic | 4,000,000 |
| Imports, scrap | 1,846,000 |
| Total | 12,646,000 |

Two and one-half million pounds of cadmium was produced in the forms of compounds, sulfides, lithopone, sulfoselenide, and cadmium oxide.

The consumption pattern for 1969 was as follows(1):

| Form | Total Consumption, percent | Application |
|---|---|---|
| Metal | 60-70 | Plating, Ni-Cd batteries, alloys |
| Sulfide pigments | 12-15 | Plastics, paints, enamels, lacquers, inks |
| Other compounds | 15-20 | Vinyl stabilizer, phosphors in TV and fluorescent lamps, semiconductor compounds, plating bath additives |

The total value of cadmium production in 1969 was about $40,000,000. There has been and will undoubtedly be more effort on the part of environmentalists to force substitution of other materials for many uses of cadmium owing to its acknowledged toxicity.

What effect this will have on future cadmium markets will depend on whether technical and engineering forces can convince lawmakers that perfectly safe practices for containing cadmium toxicity have been developed and are readily applicable.

## Raw Materials and Processes

The starting material for cadmium-recovery processes are by-products of other metal-production operations, all involving zinc. These are

(1) Fumes and dusts from the roasting and sintering of zinc concentrates

(2) Zinc metal containing relatively high concentrations of lead and cadmium

(3) Dusts from the smelting of lead-zinc ores or copper-lead-zinc ores

(4) Purification sludge from zinc electrowinning plants.

### Cadmium From Zinc Concentrates

In the recovery of zinc from zinc concentrates by the retort process, zinc sulfide concentrates are roasted, sintered (see zinc section), and introduced into retorts with reducing agents such as coal or coke. When the mixture is heated, the zinc oxide is reduced to zinc metal which is volatilized, condensed, and cast into ingots. Unless special provisions are taken, much of the cadmium and lead almost always present in zinc concentrates would accompany the zinc. Figure 23 outlines a process used to separate these elements from the zinc and at the same time

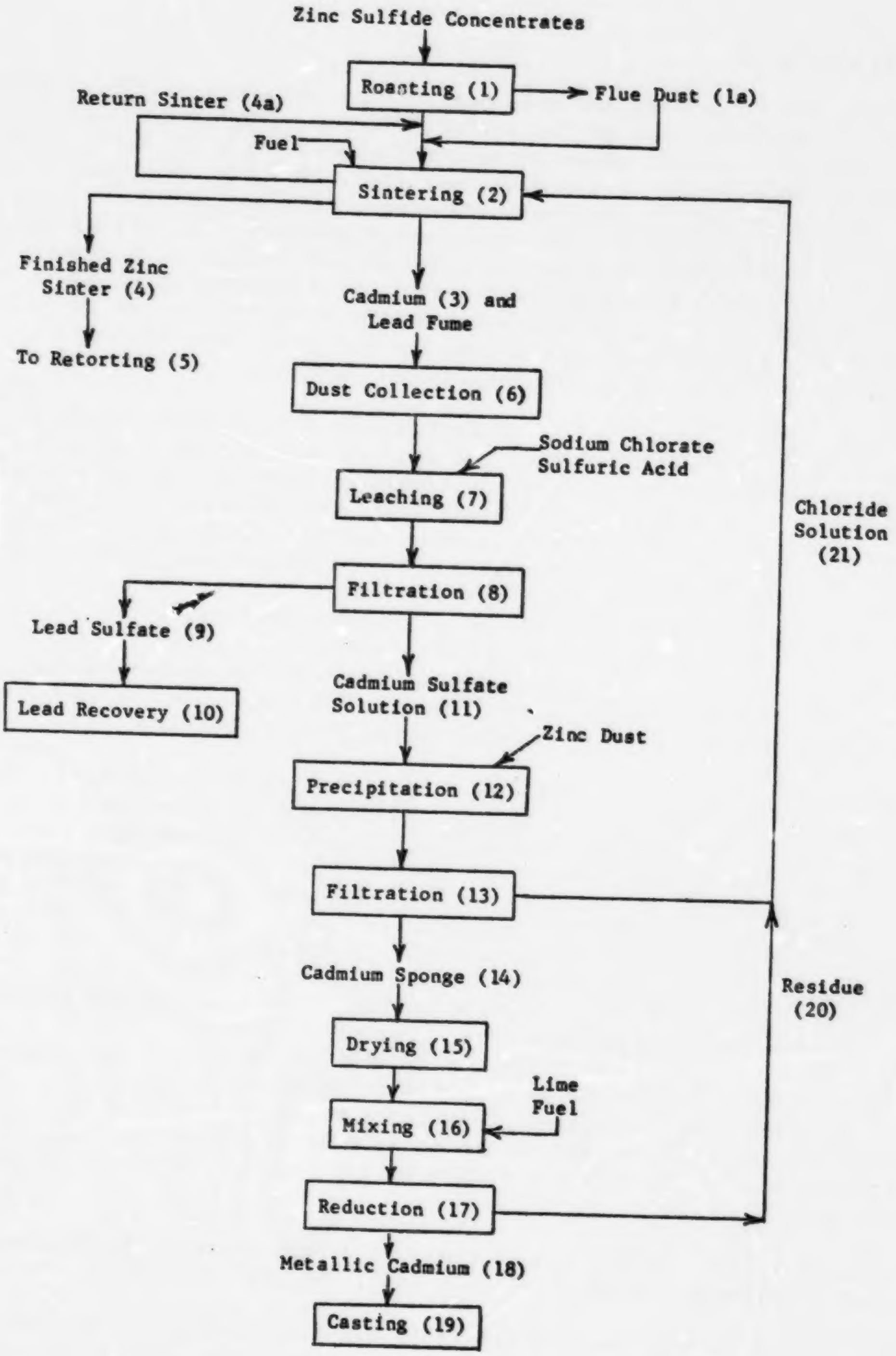


FIGURE 23. CADMIUM RECOVERY IN THE ZINC RETORT PROCESS(18)

recover cadmium.

Roasting (1) is done in multiple-hearth furnaces under oxidizing conditions to eliminate most of the sulfur. At the temperature of the roasting operation, cadmium tends to volatilize preferentially and concentrates to some extent in the flue dust (1a). This is collected in suitable equipment such as cyclones, baghouses, and electrostatic precipitators and is returned to join the roasted product. The roasted concentrates and flue dust are then charged onto the surface of a sintering machine (2) (a travelling grate furnace) which transports a bed of the material about 1 foot deep beneath a burner where the charge is ignited. Suction boxes beneath the grate draw the hot gases down through the charge as it travels from the feed to the discharge end.

The objective of sintering is to agglomerate the calcine, remove residual sulfur, and remove most of the lead and cadmium from the zinc. This lead-cadmium removal is accomplished by chloridizing the charge with the zinc chloride solution (21) returned from filtration step (13) or by the addition of sodium chloride solution. Under proper conditions of temperature and chloride addition, cadmium and lead chloride (3) volatilize from the charge and are drawn down through the bed and into the fume-collecting facilities for subsequent treatment. The sintered zinc oxide product (4) is sent to the retorting furnaces (5) for the recovery of zinc metal. In some cases, the lower few inches of the sintered bed of material, which may still contain some lead or cadmium, is separated and recirculated through the sintering operation (4a).

After collection (6) the fumes and dusts are leached (7) with dilute sulfuric acid and sodium chlorate. The purpose of the sodium chlorate is to ensure the complete dissolution of cadmium sulfide which would otherwise remain undissolved. In the leaching operation, cadmium and lead are converted to sulfates and/or chlorides. Cadmium sulfate and chloride remain in solution, but lead is almost completely converted to insoluble lead sulfate. This compound, together with other insoluble materials (quartz, silicates, etc.) is filtered out and sent to lead recovery. The solution of cadmium sulfate (and/or chloride) (11) is then treated with powdered zinc to precipitate cadmium (12). Precipitation is carried out with a deficit of zinc, so that the resulting cadmium will be as zinc free as possible. The slurry is filtered (13). The solution from filtration, containing practically all of the zinc added and about 10 percent of the cadmium as chlorides and sulfates, is returned to the sintering operation to provide the necessary chloride ion (21).

The filter cake, called sponge (14), if properly prepared, will contain about 30 percent moisture and only small amounts of lead and zinc.

This sponge is then steam dried (15), mixed with coal or coke and lime (16), and transferred to a retort furnace where the cadmium is reduced to metal, vaporized, recondensed, and cast into required shapes (17, 18, 19). Residue from the reduction furnace or retort containing some cadmium (20) is returned to the sintering operation.

## Cadmium From Zinc Metal

Some zinc made by the retort process contains both cadmium and lead in appreciable quantities. An example is the so-called prime Western zinc which may contain about 1.5 percent lead and several tenths of a percent cadmium. Such a material can be highly refined by the process shown in Figure 24. This process involves two fractionation stages, each at different temperatures. In the first, operated at a temperature in excess of 1000 to 1150 C, cadmium and zinc are boiled off, leaving a high lead-zinc alloy. The cadmium-zinc vapors are condensed and refractionated (2) at about 800 C. In this operation, cadmium is volatilized and a high-purity zinc product is withdrawn at the bottom of the fractionation column.

The cadmium product from this process generally requires further treatment by additional volatilization or chemical means.

## Cadmium Recovery From Lead Smelter Dusts

Smelter dusts, which customarily contain about 5 percent cadmium or less, as produced, may be treated in several ways to recover cadmium. Figure 25 shows three typical routes. In the first route (left side of Figure 25), the starting material is dusts from the smelter baghouses (1). In the case of burned baghouse dusts, the dusts are collected in bag filters and dropped into masonry or refractory chambers called cellars where they are ignited and allowed to oxidize by burning or smoldering. This material, after continued burning, will contain about 15 percent cadmium, 15 percent zinc, and 50 percent or more of lead. This is sent to a lead smelter where it is refumed (1a) in a so-called "Godfrey" furnace with fuel and limestone at a temperature regulated to more or less selectively volatilize cadmium. The fume collected in a baghouse (2) typically may contain up to 55 percent cadmium and about 15 percent each of lead and zinc. This material (3) is generally sent to an electrolytic zinc refinery for further treatment.

Another route is shown in the center column of Figure 25. By this route, the baghouse dust containing about 3 to 4 percent cadmium is refumed in a reverberatory furnace in several batch stages (5) in order to obtain a fumed product of optimum grade for subsequent processing (6). This fume, which may contain 40 to 45 percent cadmium is contacted (7) with water and oxidizing agents ($KMnO_4$ and $NaClO_3$) in a ball mill and leached by agitation with additional sodium chlorate, ferrous sulfate, and sulfuric acid. The purpose of the oxidizing agents and the ferrous sulfate is to ensure that cadmium is all dissolved and that arsenic is oxidized and precipitated as ferric arsenate. The slurry is filtered (9);

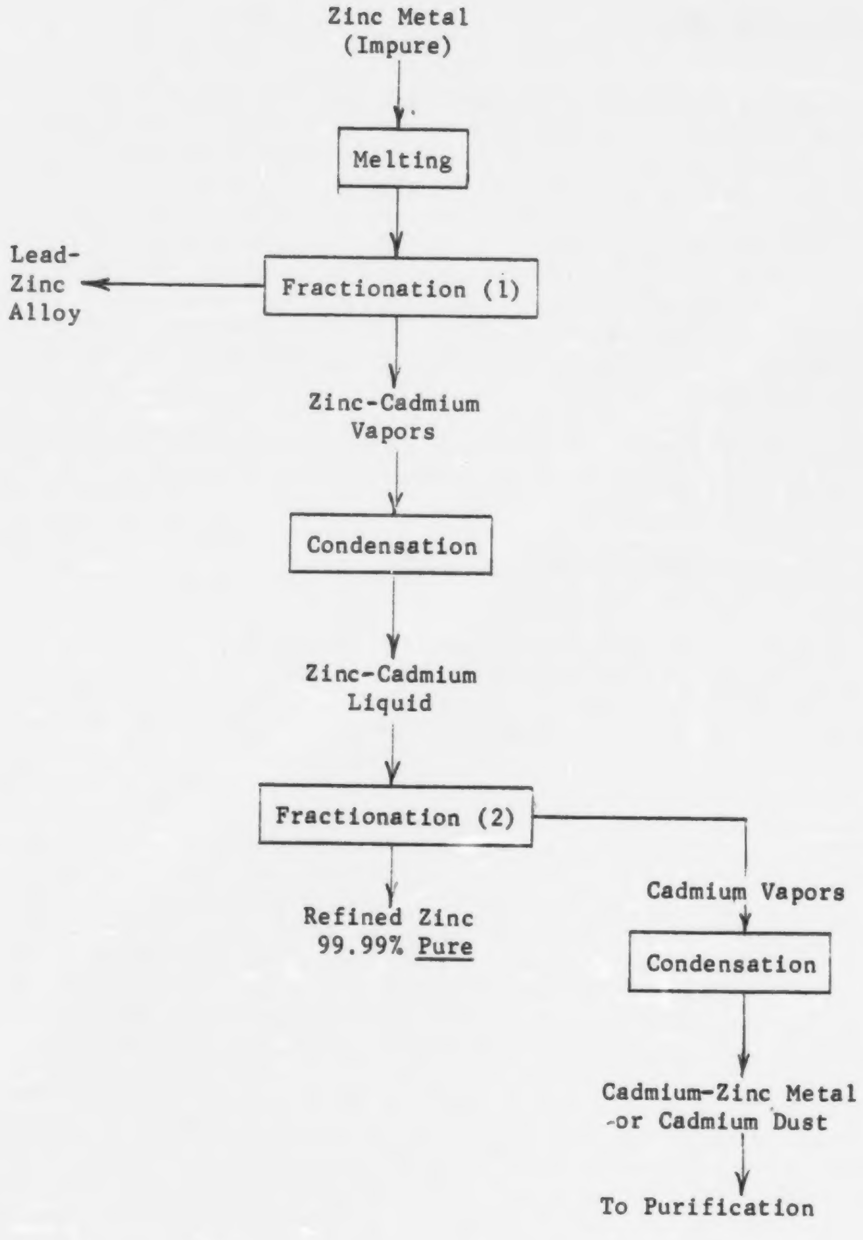


FIGURE 24. CADMIUM RECOVERY FROM ZINC METAL

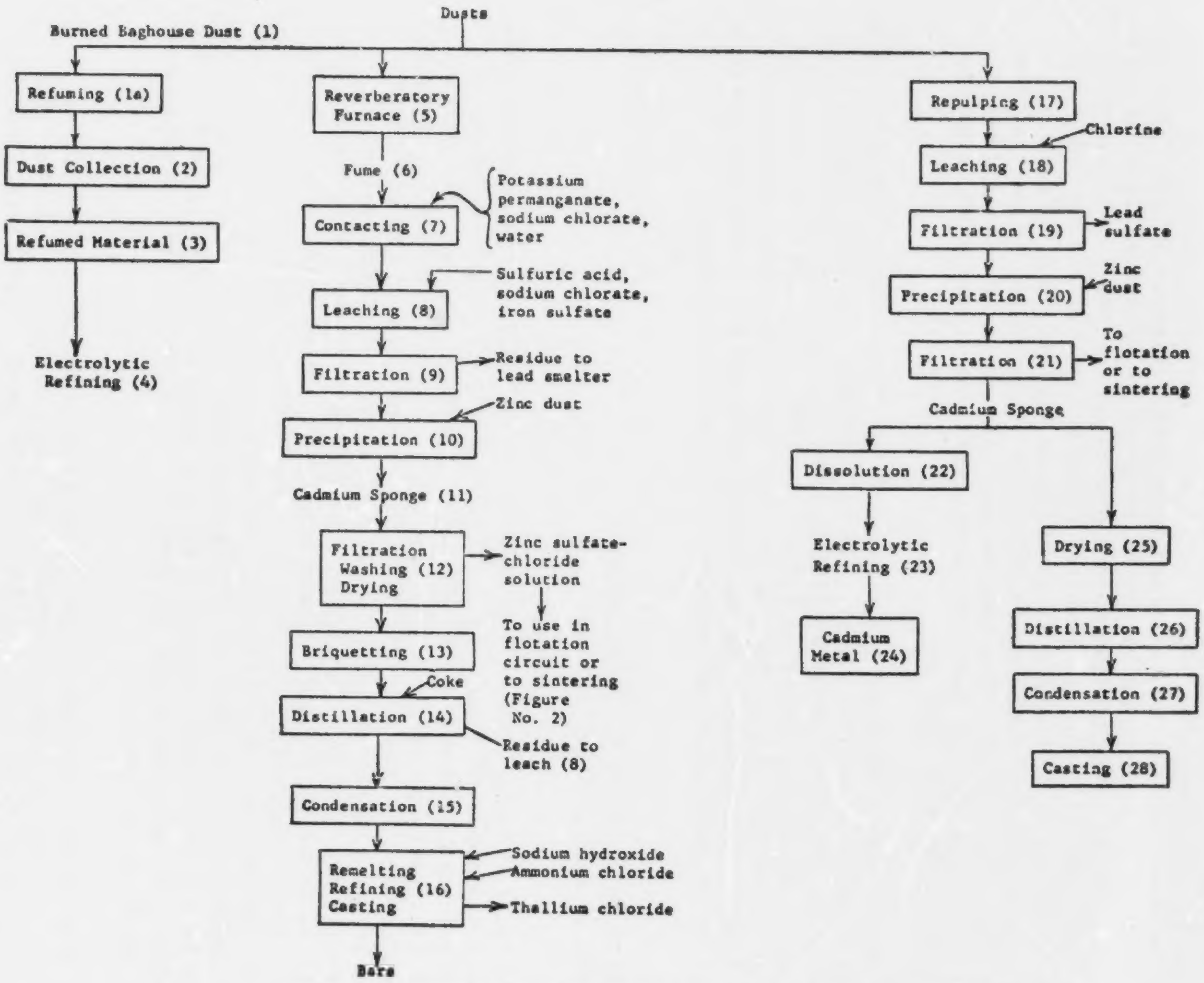


FIGURE 25. CADMIUM RECOVERY FROM LEAD, ZINC, OR COPPER SMELTER DUSTS

the residue, consisting of lead sulfate and ferric arsenate, is sent back to lead smelters.

Precipitation with zinc dust (10) under controlled conditions of acidity produces a fairly high-grade "sponge" (11). This is filtered, washed by repulping with water, refiltered, and dried (12). The filter cake is then granulated and formed into small briquettes (13). The briquettes are then retorted batchwise in graphite crucibles (14) to volatilize cadmium. The cadmium vapors are condensed and the liquid metal cast into bars. These are remelted under a layer of sodium hydroxide flux in electric furnaces. If thallium is present, the sodium hydroxide flux is removed and ammonium chloride is added to remove thallium from the cadmium (15). The cadmium is then recovered with sodium hydroxide flux and the purified metal, which may contain 99.95 percent of cadmium, is cast into bars.

The third route, shown at the right side of Figure 25 is also applicable to lead and zinc smelter fumes. In this process the fume or dust is leached by repulping in water (17) and the slurry is treated with chlorine gas. Subsequent steps of filtration (19), precipitation, and isolation of cadmium sponge (20 and 21) are similar to those previously described. The resultant sponge may be subsequently treated by electrolytic or pyrometallurgical methods to produce pure cadmium.

### Cadmium Recovery From Purification Sludge in Zinc Electrowinning

The electrowinning process for zinc is described in the section of this report dealing with that metal. The successful electrodeposition of zinc requires extremely pure solutions. Cadmium, among other metals, such as copper, nickel, cobalt, and iron, must be virtually completely removed. In zinc metallurgy, both copper and cadmium are eliminated from solution by treating the zinc electrolyte with powdered zinc. Generally this is done stagewise. In the first stage, only enough zinc metal is added to precipitate copper, which, being more noble than cadmium, reacts preferentially with the zinc powder. After removal of the copper precipitate by filtration, the zinc electrolyte is then treated with additional zinc dust to precipitate the cadmium. This precipitate, high in zinc, contains virtually all the cadmium originally in the electrolyte and constitutes the so-named purification sludge. Its processing is shown in Figure 26.

This purification sludge (1) is first allowed to oxidize (2) in air, with or without heating, to render the cadmium readily soluble. The oxidized material is then leached (2) with spent electrolyte from the electrolysis step. After filtration (4) to remove insoluble copper introduced from the zinc electrolyte, the filtrate is stage-treated with zinc dust (6, 7, 16, 17, 18. 19) to minimize zinc concentration in the cadmium sponge (8). This sponge containing about 80 percent

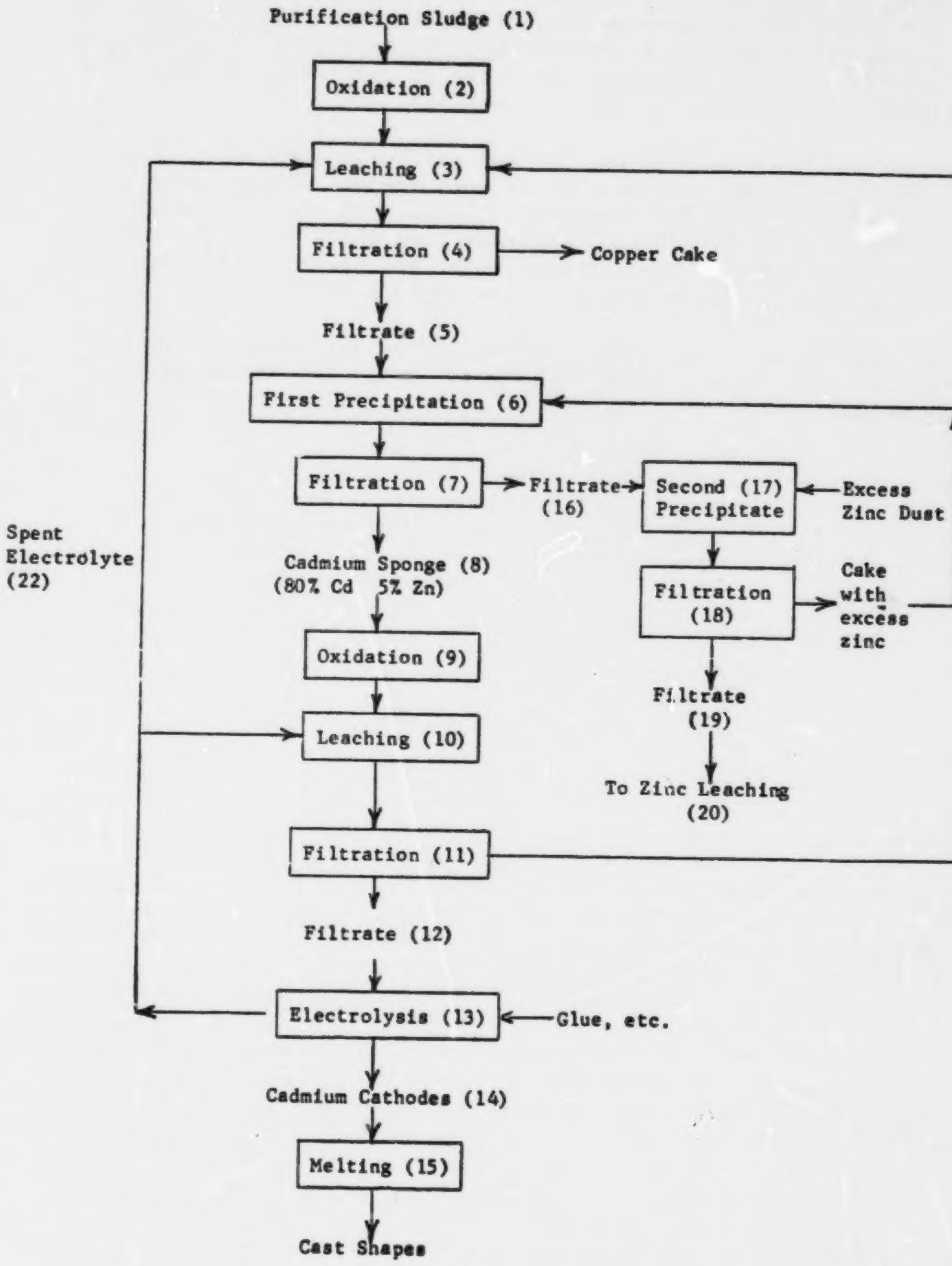


FIGURE 26. CADMIUM RECOVERY FROM PURIFICATION SLUDGE OF ZINC ELECTROWINNING OPERATIONS(19)

cadmium with 5 percent zinc, is again oxidized by steam drying to enhance the solubility of cadmium (9). It is leached (10) in spent electrolyte from the electrolysis circuit and filtered (11). The filtrate (12), containing about 200 grams per liter of cadmium as sulfate, is then electrolyzed to produce cadmium cathodes.

Electrolysis (13) is carried out in banks of cells similar to zinc cells, described under that section of this report. These cells are fitted with lead anodes and aluminum cathodes. In the electrolysis, cadmium plates onto the aluminum cathodes from which it is periodically stripped. After passage through the cells, the spent electrolyte is returned to various leaching stages in the circuit (22).

Stripped cathode metal is washed, dried, and melted under a flux and cast into various shapes, including ingots, balls for use as electroplating anodes, etc.

# SECTION X

## BY-PRODUCT GOLD AND SILVER

### Recovery of Gold and Silver From Copper Ores[4,11,20]

Figure 27 outlines routes for the recovery of silver and gold.

Silver and gold follow copper through all stages of concentration, smelting, and fire refining (1). When copper is refined electrolytically, however, these metals together with selenium, tellurium, etc., collect as the finely divided solids in the electrolytic tank. These are called slimes (2) (see the section on copper). These slimes, as produced, contain high percentages of fine copper and are first leached in hot dilute sulfuric acid (3) to dissolve excess copper, and some tellurium and selenium, away from the silver and gold (4). Typically, such leached slimes will contain about 10,000 ounces of silver per ton, with varying proportions of gold, lead, selenium, arsenic, antimony, etc., depending on the characteristics of the original ore (5). The treated slimes are then smelted in a small reverberatory furnace, called a Doré furnace (6), with various fluxes such as limestone, borax, fluorite, silica, etc., selected to produce a fluid slag of the base metals so that they may be separated from the bulk of the molten silver and gold. This slag (7) normally contains significant amounts of gold and silver, and to recover these values it is usually returned to the copper smelter. The gold and silver alloy, now rid of most of its base metal and metalloid impurities, is called Doré metal (8). Typically, such an alloy will contain 90 or more percent of silver, gold, platinum, and a small amount of copper. The molten Doré metal is cast into small anodes (10). These are electrolyzed in small specialized cells in nitrate solution (11). Two main types of electrolytic cells are used. In one type, the Thum cell, carbon cathodes constitute the floor of the cell, and the impure silver anodes are suspended in a shallow receptacle with a cloth bottom. On electrolysis in this type of cell, the silver dissolves anodically and is deposited in small crystals on the bottom cathode. These crystals are raked either manually or mechanically from the cell, washed, and dried (13). During the electrolysis, gold and platinum do not dissolve but collect as slimes on the cloth bottom of the anode receptacle (12). These are sent to further processing for the recovery of these metals.

The electrolytically refined silver crystals (13) which will exceed 99.9 percent purity are subsequently melted and cast into bars weighing about 100 pounds. Another type of cell, called the Moebius cell, is also used in silver refining. In this cell the anodes are enclosed in cloth bags and suspended alternately between cathodes. During electrolysis in the nitrate solution, silver is anodically dissolved and deposits as

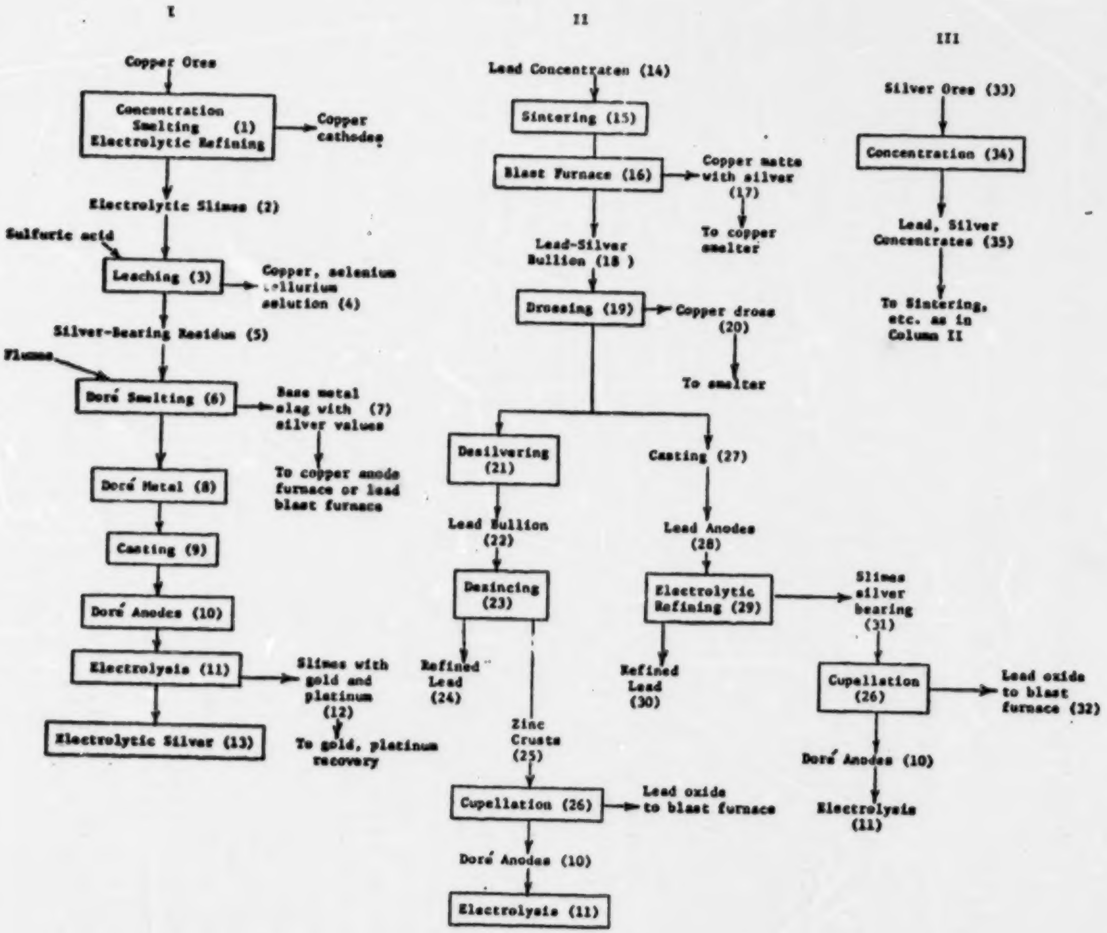


FIGURE 27. DIAGRAM SHOWING STEPS IN THE RECOVERY OF BY-PRODUCT GOLD AND SILVER

loosely adherent crystals on the cathodes. These are periodically mechanically scraped off into a basket on the bottom of the cell. The gold and platinum slimes in the Moebius cell are retained in the anode bags.

## Recovery of Gold and Silver From Lead Concentrates

The recovery of gold and silver from ores in which lead and zinc are the major components by weight is less straightforward than the recovery from copper ores. Silver follows copper through to the electrolytic refining step in copper metallurgy. In lead metallurgy, however, silver may follow several routes. After lead concentrates are sintered (15) and smelted in the blast furnace (16), a portion of the silver will accompany the copper matte that is normally formed. This matte (17) is returned to copper smelters for the recovery of both silver and copper as outlined in Column I of Figure 27. Much of the silver, however, accompanies lead in a bullion (18). Bullion from most ores contains enough gold and silver to make their extraction profitable. In addition, it contains undesirable impurities such as copper, zinc, tin, antimony, and arsenic which must be removed by refining. The processing steps for refining lead will vary with the composition of the impure bullion and the end product desired. The steps shown in Column II from the drossing step on are typical.

Drossing (19) consists of holding the molten bullion at a temperature just above the melting point, during which operation copper rises to the top and is skimmed off. The last traces of copper are removed by adding sulfur. The copper dross is returned to a copper smelter for copper recovery and the recovery of whatever silver may have accompanied the copper dross. Arsenic, antimony, and tin are subsequently oxidized and are also skimmed from the surface of the lead.

After drossing, two routes are available for the production of refined lead. One, essentially fire refining, includes a silver- and gold-recovery procedure involving the addition of zinc metal to the molten lead (21, 22, 23, 24, 25, 26). When zinc is added in the desilvering step, the precious metals alloy with the zinc and rise to the surface. The last traces of zinc in the lead are removed either by vacuum distillation or by fluxing with caustic soda (23). The zinc fraction or zinc crusts (25) removed from the lead are then "cupelled" (26) in a small reverberatory furnace under strongly oxidizing conditions to convert the lead to molten lead oxide which carries off other materials besides gold and silver. Lead oxide with its burden of impurities such as zinc, arsenic, antimony, etc., is returned to the lead blast furnace. The molten gold and silver remains in the cupel furnace as Doré metal, and is cast into anodes for treatment as shown in Column I of Figure 27 (10,11).

Another path for producing refined lead after the drossing operation is by electrolytic refining (29) which is described in the section of this report dealing with lead. Electrolytic refining is generally employed when undesirably high concentrations of bismuth are present. During the electrolysis of lead, silver and gold, as in copper electrolysis, separate as slimes. These are collected and subjected to cupellation (26) and electrolysis (27) as described previously.

## Refining of Precious Metals

The impure gold recovered by any of the above processes is refined by treatment in the so-called Doré furnace. In this operation, the material is melted with appropriate fluxes (soda ash, borax, silica, etc.) under oxidizing conditions to produce a gold-base alloy which may still contain silver and the platinum-group metals and a slag which will contain impurities such as copper, zinc, etc.

If platinum-group metals are absent or virtually so, the Doré metal is purified, while still molten, by the Miller process, in which chlorine is bubbled through the charge. This treatment volatilizes base metals which may be present and converts silver to molten silver chloride salt which rises to the top of the melt and can be poured or skimmed from the gold. Refined gold made by this process generally contains about 99.6 percent gold, and is suitable for many purposes.

If platinum metals are present or if higher purity is desired, the Doré metal is cast into small anodes and electrolyzed in chloride solution by a miniaturized method analogous to the refining of copper by electrolysis. In this process, the Wöhlwill process, gold is electrolytically oxidized as the anode passes into solution and is deposited in pure form on the cathode. The resulting cathode is melted and cast into bars of $99.9^+$ percent purity. In the Wöhlwill process, silver is also electrolytically oxidized at the anode, but is quickly and almost completely converted to insoluble silver chloride.

# SECTION XI

## THE ARSENIC INDUSTRY

### Size and Characteristics

The production of arsenic in the United States is almost exclusively as a by-product from the smelting of copper and lead ores. In the roasting and smelting of such ores, arsenic oxidized to $As_2O_3$, is volatilized, and is recovered in fumes and flue dust. These contain varying amounts of the trioxide (up to 30 percent) associated with the oxides of other metals such as copper, lead, antimony, zinc, or tin, and various other particulate materials.

The most marketable form of arsenic is the pure trioxide, with little demand for pure elemental metallic arsenic. In the United States, the only primary metal producer now making either arsenic trioxide or arsenic is the Tacoma smelter of the American Smelting and Refining Company (the only producer in 1969).(1) In earlier years Anaconda also produced arsenic in Montana. No production data have been published in recent years. United States imports in 1969 amounted to 18,171 tons and had decreased from about 27,000 tons in 1967.

The method of producing the trioxide from smelter flue dusts consists of sequential volatilization operations, with operating temperature being the method of controlling the selective volatilization of the oxide from flue dusts and the purity of the product.

Thus, processing consists of roasting the flue dusts to volatilize the contained $As_2O_3$, which concentrates in the fume from the roasting operation. The collected fume is again heated in a reverberatory furnace, and the fume from this operation is passed through a series of chambers to collect fractions of various purity from the volatilized furnace output. The purity level is determined by cooling-chamber temperature. These steps are indicated in Figure 28.

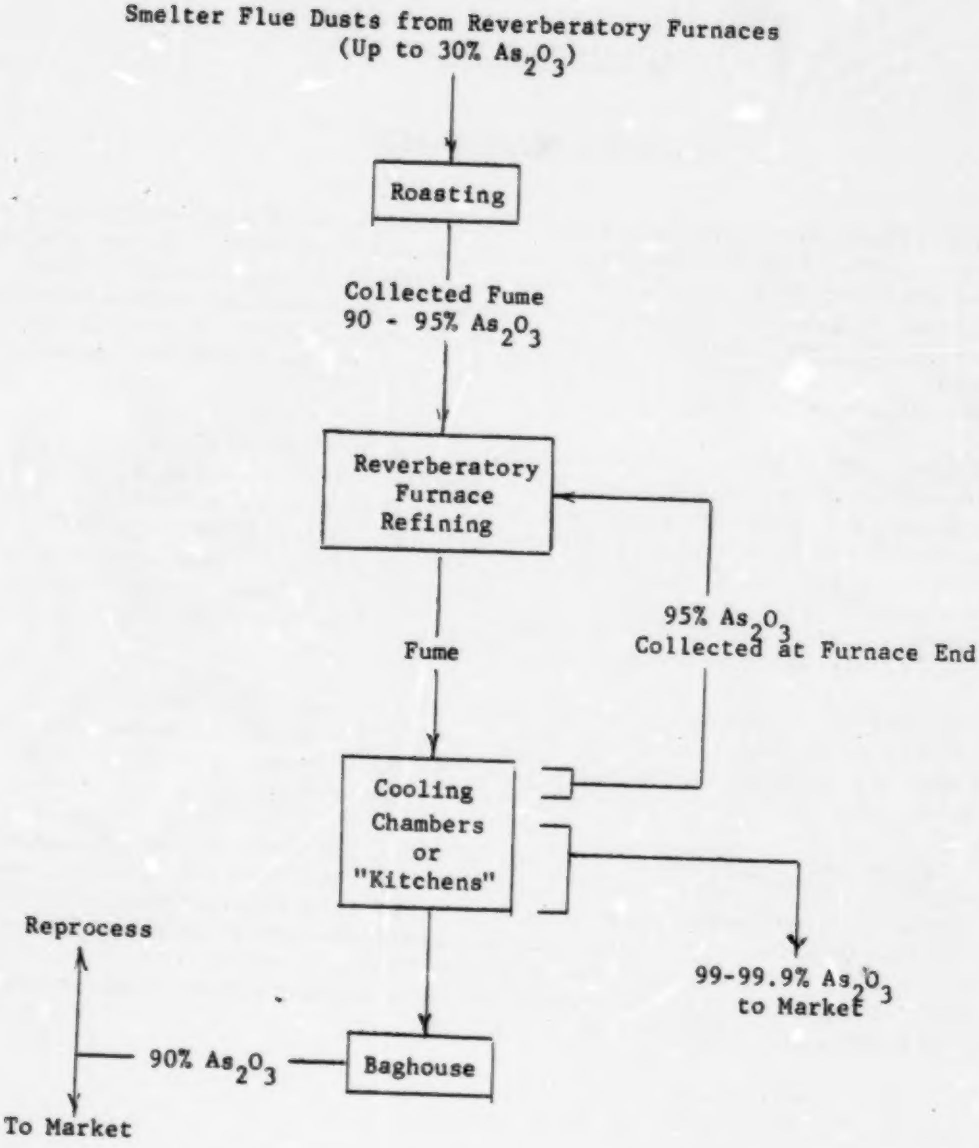


FIGURE 28. STEPS IN THE CONCENTRATION AND PURIFICATION OF ARSENIC TRIOXIDE(21)

## SECTION XII

# THE PRIMARY ANTIMONY INDUSTRY

### Size and Characteristics

The primary antimony industry is relatively small. In 1969, total primary antimony production in the United States was 13,203 tons, about 17 percent of world production.(1) Salient production data are given in Table 25. The consumption and uses of antimony as metal and compounds are shown in Table 26.

Facilities producing antimony in the United States and their activities are as follows:

| | |
|---|---|
| Sunshine Mining Company Coeur D'Alene, Idaho | Mining, concentrating, and electrowinning of antimony metal |
| Several properties adjacent to above | Mining |
| Stampede Mine, Kantishna District, Alaska | Mining and concentration with export of concentrates |
| Gold Creek Mine Elko Co., Nevada | Mining, shipment of ore to National Lead Smelter, Laredo, Texas |
| Smokey Claims Humboldt Co., Nevada | Mining, shipment of ore to National Lead Smelter, Laredo, Texas |
| Stibnite Mine, Souders Co., Nevada | Idle in 1969, but sold to the U.S. Antimony Corp. |
| Wells Fargo Mine, Stevens Co., Washington | Development work with stockpiling of antimony silver ore |
| Various lead and lead-zinc mines with antimony as by-product | See section on lead |
| National Lead Co. Smelter, Laredo, Texas | Pyrometallurgical production of antimony metal and antimony oxide |
| American Smelting and Refining Co. | Principal producer of by-product antimony at Omaha, Neb., and Perth Amboy, N.J., plant |

## TABLE 25. SALIENT ANTIMONY STATISTICS(1)

(Short tons)

| | 1965 | 1966 | 1967 | 1968 | 1969 |
|---|---|---|---|---|---|
| United States: | | | | | |
| Production: | | | | | |
| Primary: | | | | | |
| Mine | 845 | 927 | 892 | 856 | 938 |
| Smelter [1] | 12,389 | 14,539 | 12,466 | 12,489 | 13,203 |
| Secondary | 24,321 | 24,258 | 23,664 | 23,699 | 23,840 |
| Exports of ore, metal and alloys | 14 | 29 | 82 | 109 | 207 |
| Imports, general (antimony content) | 14,879 | 19,712 | 17,419 | 17,343 | 17,032 |
| Consumption [1] | 16,919 | 19,681 | 17,350 | 18,520 | 17,843 |
| Price: New York, average cents per pound | 45.75 | 45.75 | 45.75 | 45.75 | 57.57 |
| World: Production | 69,456 | 67,627 | 63,565 | 67,737 | 72,059 |

[1] Includes primary antimony content of antimonial lead produced at primary lead smelters.

## TABLE 26. INDUSTRIAL CONSUMPTION OF PRIMARY ANTIMONY IN THE UNITED STATES, BY CLASS OR MATERIAL PRODUCED(1)

(Short tons, antimony content)

| Product | 1965 | 1966 | 1967 | 1968 | 1969 |
|---|---|---|---|---|---|
| METAL PRODUCTS | | | | | |
| Ammunition | 36 | 154 | 209 | 156 | 115 |
| Antimonial lead | 6,382 | 6,285 | 5,539 | 6,817 | 6,723 |
| Bearing metal and bearings | 821 | 731 | 653 | 755 | 758 |
| Cable covering | 68 | 164 | 141 | 178 | 55 |
| Castings | 76 | 62 | 54 | 46 | 33 |
| Collapsible tubes and foil | 49 | 44 | 31 | 50 | 56 |
| Sheet and pipe | 104 | 107 | 118 | 105 | 105 |
| Solder | 244 | 155 | 184 | 255 | 242 |
| Type metal | 642 | 515 | 382 | 423 | 541 |
| Other | 214 | 219 | 223 | 258 | 137 |
| Total | 8,636 | 8,436 | 7,534 | 9,043 | 8,765 |
| NONMETAL PRODUCTS | | | | | |
| Ammunition primers | 16 | 27 | 30 | 33 | 37 |
| Fireworks | 46 | 50 | 43 | 37 | 30 |
| Flameproofing chemicals and compounds | 1,971 | 3,188 | 3,454 | 2,774 | 2,096 |
| Ceramics and glass | 1,853 | 2,074 | 1,884 | 2,037 | 2,108 |
| Matches | W | ------ | ------ | ------ | ------ |
| Pigments | 855 | 832 | 665 | 859 | 722 |
| Plastics | 1,469 | 2,224 | 1,785 | 2,318 | 2,558 |
| Rubber products | 477 | 870 | 948 | 440 | 433 |
| Other | 1,596 | 1,980 | 1,007 | 979 | 1,094 |
| Total | 8,283 | 11,245 | 9,816 | 9,477 | 9,078 |
| Grand total | 16,919 | 19,681 | 17,350 | 18,520 | 17,843 |

W Withheld to avoid disclosing individual company confidential data; included with, "Other."

| | |
|---|---|
| McGeen Chemical | Antimony oxide producer |
| M and T Chemical Co. | Antimony oxide producers |
| Harshaw Chemical Company | Antimony oxide producers |
| Foote Mineral Co. | Antimony sulfide producers |
| Hummel Chemical Co. | Antimony sulfide producers |

## Raw Materials and Processes

The most important antimony mineral is stibnite, $Sb_2S_3$, although various oxide minerals may be associated with stibnite deposits in small amounts. Antimony ores, containing stibnite and minor amounts of oxide minerals, occur in a few instances in deposits in which antimony is a major value, as in Idaho and Nevada. From such deposits, it is possible to obtain high-grade ore (+40 percent antimony), by selective mining, and concentrates containing 15 to 30 percent antimony. Most of the domestic antimony production comes from imported ores treated at the Laredo, Texas, antimony smelter. Other production is based on antimony derived from the processing of lead ores.

## Mining and Concentration

Only a few mines are operated principally for the recovery of antimony alone and these are generally small. Most of the antimony ore bodies are not amenable to large-scale mining methods employed in the mining of copper, zinc, and lead, owing to the size, irregularity, and distribution of the ore veins. These are mined selectively, ore and waste being removed selectively to prevent dilution. A larger scale, open-pit gold-tungsten-antimony mine was formerly operated in Idaho, but this was closed down in 1969. The bulk of the mine production of antimony in the United States is from the Sunshine silver mine in Idaho. This is a unique operation in which antimony in the silver concentrates is leached and won electrolytically as high-purity metal. Most of the primary antimony mined in the United States is a by-product of lead ores.

Concentration of antimony ores in this country now appears to be chiefly by selective mining and hand picking. Flotation concentration has been employed successfully in the past for complex ores in which antimony was a major coproduct.

## Metal-Reduction Processes

The methods selected for the production of antimony metal or oxide are largely determined by the grade of the ore or concentrates. The lowest grade ores or concentrates (5 to 25 percent antimony) are generally treated by volatilization processes; those containing 25 to 40 percent antimony are smelted in a blast furnace; high-grade ores containing 45 to 60 percent antimony may be treated by a process called liquation, in which the antimony is reduced, melted, and drained from the gangue material; special concentrates, such as the silver-antimony concentrate produced by the Sunshine Mining Company in Idaho, are treated by leaching and electrowinning. Condensed oxides from volatilization processes, liquated antimony sulfide, and some intermediate-grade ores are smelted in reverberatory furnaces.

Volatilization. Volatilization processes depend on the volatility of antimony trioxide and are especially suitable for low-grade ores (5 to 25 percent antimony).

In the volatilization process, the ore is heated with carbonaceous material under controlled conditions of temperature and aeration to convert stibnite ($Sb_2S_3$) to volatile antimony trioxide ($Sb_2O_3$). The oxide is condensed and recovered in suitable dust-collecting equipment. After collection, the oxide is reduced to metal by subsequent furnacing with coke under reducing conditions. By careful manipulation of conditions, volatilization processes are capable of producing high-purity oxides in a single step.

Liquation. The liquation process requires high-grade ores running 50 to 60 percent antimony. The objective of liquation is to melt, selectively, the stibnite ($Sb_2S_3$) and to drain it from the gangue materials. The product, antimony sulfide, may be sold as such or it may be subsequently converted to antimony metal. The residues resulting from liquation still contain significant quantities of antimony and these are generally treated by volatilization processes for more complete recovery.

Liquation may be carried out on a batch basis in liquating furnaces which are simply clay crucibles with perforations in their bottoms to permit outflow of the melted antimony sulfide. Tube furnaces and reverberatory furnaces, which permit continuous operation, also may be used.

Blast Furnace Smelting. The National Lead smelting operation at Laredo, Texas, utilizes this method. The charge to the blast furnace consists of mixed oxide and sulfide ores from mines in Mexico or the United States, and by-products of other smelting operations; mattes, slags, flue dusts, or residues from lead and zinc refineries. The blast-furnace operation is somewhat similar to that of lead blast-furnace practice. A vertical or shaft furnace with a rectangular cross section is used, with low-pressure air being supplied through tuyeres. The ore and residues, charcoal, and fluxing additions are charged at the top of the furnace and the products of molten antimony metal and slag are tapped from the hearth at the bottom of the furnace. The blast-furnace process is capable of producing extremely pure metal with minimal antimony loss.

## Reverberatory Furnace Smelting

Impure oxides produced by volatilization processes, liquated antimony sulfides, residues, and ores containing antimony and impure metal may be converted to high-purity metal by reverberatory-furnace smelting, either batch or continuous. In this operation, the antimony-bearing charge is heated with coke and such fluxing materials as soda ash and sodium sulfate. Coke reduces the oxides of antimony to metal and the soda slag removes gangue minerals and sulfur. If iron is present in the charge, it reacts with sulfur to form a matte between the metal and slag. Considerable antimony is volatilized as antimony oxide during reverberatory-furnace smelting. This is collected in suitable equipment and returned to the furnace.

## Leaching-Electrolysis

Currently, primary antimony metal is being produced at the Sunshine Mining Company in Idaho by a leaching-electrolysis process. The process is depicted in Figure 29. In this process, a complex copper-antimony sulfide concentrate is leached with sodium sulfide solution which dissolves the antimony as sodium thioantimonate ($Na_3SbS_4$). The leach solution is clarified by settling and filtration, and electrolyzed in diaphragm cells to yield antimony of 93 to 99 percent purity. During the electrolysis, some sulfide sulfur is oxidized to thiosulfate or sulfate. With recirculation of the electrolyte, the concentration of these oxidized forms of sulfur would build up to the point where they would interfere with the solubilization of antimony in the leaching step. By treating spent electrolyte with barium sulfide, these sulfates are kept at acceptable levels, and the sulfide concentration is maintained. The barium sulfate and thiosulfate precipitate is filtered and heated with coal in a rotary kiln to reconstitute barium sulfide for reuse.

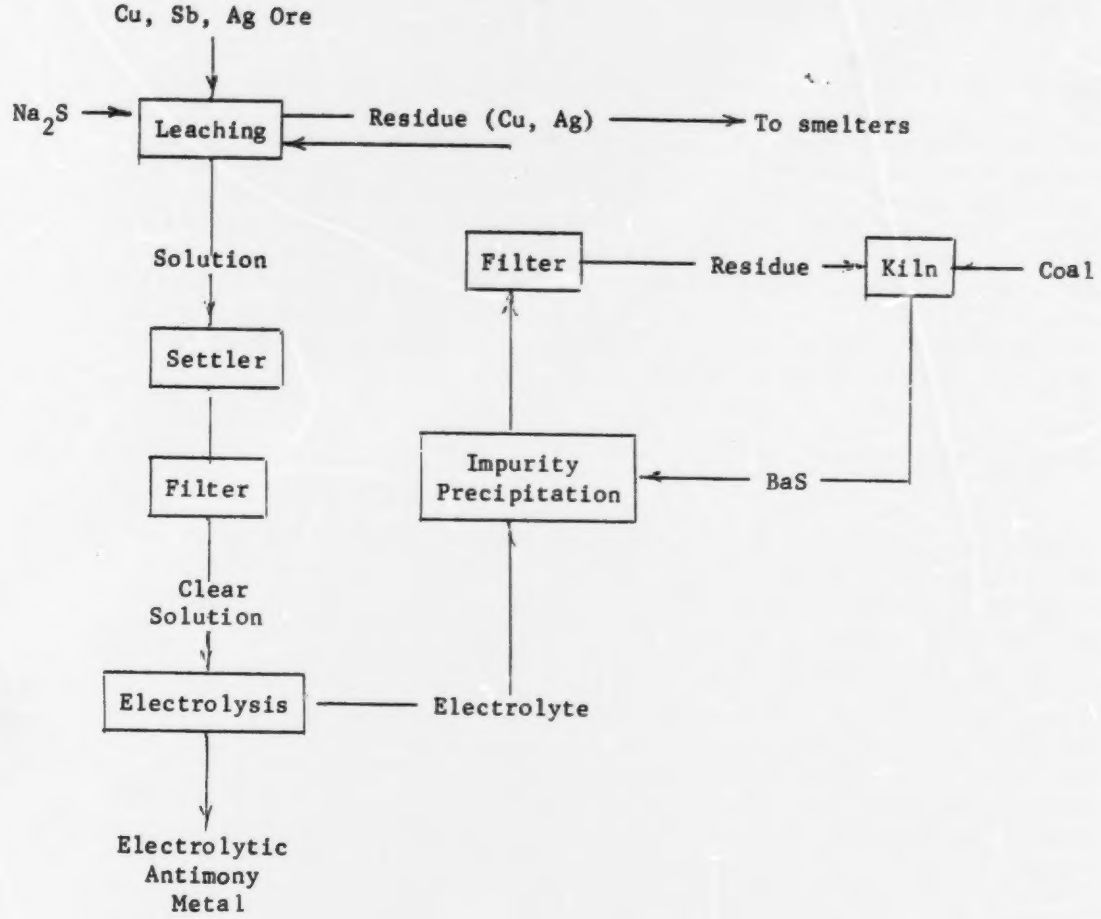


FIGURE 29. DIAGRAM OF PROCESS STEPS IN THE PRODUCTION OF ANTIMONY AT SUNSHINE MINING OPERATION

# SECTION XIII

## THE PRIMARY BISMUTH INDUSTRY

### Size and Characteristics

In 1969, three producers of bismuth were reported operating in the United States. These were the Omaha plant of the American Smelting and Refining Company; the East Chicago plant of the U.S. Smelting and Refining Company; and the Texas City Smelter and the Los Nietos (California) Refinery, both operated by the Gulf Chemical and Metallurgical Corporation.(1) No production figures are available.

The consumption and uses of bismuth are given in Table 27. Its uses in low-melting alloys include applications in fuses, temperature-sensitive devices, and mold and die materials for forming plastics and other metals. Bismuth is used as an alloying addition to cast irons, aluminum alloys, amalgams, and bearing alloys. The largest use is in cosmetics in the form of bismuth oxychloride.

TABLE 27. CONSUMPTION OF BISMUTH IN THE UNITED STATES IN 1969 (POUNDS)

| | |
|---|---|
| Low-Melting Alloys | 748,393 |
| Aluminum, Cast Iron, and Other Alloys | 523,710 |
| Pharmaceuticals and Cosmetics | 1,250,539 |
| Experimental Uses | 252 |
| Other | 9,065 |
| Total | 2,531,959 |

### Raw Materials and Processes

There is no mineable bismuth ore in the United States, and bismuth production is tied firmly to the production of copper and lead. Bismuth, present in the ores of these metals, follows them through concentration and all the preliminary steps of processing to be finally removed in lead-refining steps. In copper smelting, for example, bismuth persists with copper until the converting operation, in which much of it volatilizes with lead, antimony, etc., as fumes. These are collected and sent to lead smelters. The portion of bismuth which escapes volatilization during converting is finally removed in the electrolytic copper refinery in the slimes. Treatment of these slimes for the recovery of gold and silver leaves bismuth associated with lead. Bismuth associated with lead ore accompanies lead through all steps of processing and must be removed by special refining processes discussed in the section of this report dealing with lead.

Refining of bismuth is done by chlorination. When the bismuth has been removed from lead by the pyrometallurgical procedure, it is collected in a dross containing calcium, bismuth, magnesium, and lead. This dross is melted and chlorinated to remove calcium and magnesium as a molten chloride slag and a bismuth-lead alloy. The alloy is fluxed with molten sodium hydroxide to remove traces of arsenic and tellurium that may be present. Residual silver and gold are removed by treatment with zinc, as described in the section of this report dealing with lead. The resultant lead-bismuth-zinc alloy is then subjected to chlorination treatment with chlorine gas under controlled conditions. Zinc and lead combine with chlorine preferentially over bismuth and are removed as molten chloride slags. The molten bismuth is finally treated with air and caustic soda and cast. This method of refining is said to yield bismuth 99.999 percent pure.

During the electrolytic refining of lead, bismuth enters the slimes with any arsenic, silver, gold, or antimony that may have been present. These slimes are filtered, dried, and melted to produce a slag and metal. The metal phase is blown with air to remove arsenic and antimony. It is then cupelled, i.e., heated under oxidizing conditions, to produce a lead-bismuth slag and a Doré alloy of gold and silver. The lead-bismuth slag is reduced by carbon to form a lead-bismuth alloy which is refined by chlorination as described above.

## SECTION XIV

## WATER USAGE IN THE LEAD-ZINC INDUSTRY

Nineteen firms responded to the canvas of the lead-zinc industry for information on water usage. The data are shown in Table 28, which indicates the types of operations reported on (mine-mill, smelter, etc.) and the total intake and discharge volumes.

Data on water usage, recirculation practices, and usage per ton of metal reported by lead and zinc producers are given in Table 29.

The water-use data for lead and zinc mines permits the following general conclusions and observations.

(a) Intake and discharge quantities are related to a number of factors. The principal determinants are plant capacity and the availability (and presumably the cost) of water.

(b) The overall recycle ratio of total water use to raw water intake is generally low (1, no recycle, to 1.5, 50 percent recycle), although in one case (No. 14, Table 29) a recycle ratio of 2.6 was reported.

(c) The volume of water reported used in processing and auxiliary operations per ton of metal for both lead and zinc mine-concentrator combinations ranged between 10,660 to 21,600 gallons in a reasonably close pattern. The spread is probably attributable to differences in ore grade and slight variations in plant practice.

(d) There is wide scattering in the data showing the distribution of intake water to process, cooling, etc. Specific reasons for this are not clearly discernible from the reports supplied to the study. The variability is associated with plant size and a host of other factors such as location, ore grade, climate conditions, water availability, cost, etc.

The data for zinc and lead smelter discharges also reflect the effects of such variables.

Recycle ratios tend to be high in most of the lead and zinc smelter operations, reflecting the large percent usage for cooling, the usual operation of cooling towers and cooling-water circuits, and the trend to economize on the use of water treated chemically to protect tubes and piping.

In five of the smelter operations included in the data listed, sulfuric acid plants were operated in association with the smelters, and the operation of these plants apparently exerts no consistent recognizable

TABLE 28. SAMPLE OF LEAD- AND ZINC-PRODUCING OPERATIONS RESPONDING TO SURVEY

| Products and By-products | Operations |  |  |  |  |  | Intake, MGY(a) | Discharge, MGY(a) |
|---|---|---|---|---|---|---|---|---|
|  | Mine | Mill | Smelter | Refinery | Power Plant | Acid Plant |  |  |
| Zn, Pb, Cu, Ag, Au | X | X | -- | -- | -- | -- | 257 | 257 |
| Zn, Pb | X | X | -- | -- | -- | -- | 303 | 303 |
| Zn, Pb, Cd, Ag, Au | X | X | -- | -- | -- | -- | 1,300 | 122 |
| Zn | -- | -- | X | X | -- | -- | 72 | 19.6 |
| Zn | -- | -- | --- | X | X | X | 693 | 341 |
| Zn, Cd | -- | -- | X | X | X | X | 4,130 | 4,077 |
| Pb, Zn, Ag | X | X | -- | -- | -- | -- | 330 | 330 |
| Pb, Zn, Ag | X | X | -- | -- | -- | -- | 238 | 238 |
| Pb, Zn, Ag, Cu | X | X | -- | -- | -- | -- | 357 | 318 |
| Pb, Zn, Ag, Cd | X | X | -- | -- | -- | -- | 474 | 473 |
| Pb, Zn, Cd | X | X | -- | -- | -- | -- | 350 | 348 |
| Pb, Ag | X | X | -- | -- | -- | -- | 99 | 0 |
| Pb | X | X | -- | -- | -- | -- | 2,900 | 2,470 |
| Pb, Cu, Cd | -- | -- | X | -- | -- | -- | 894 | 763 |
| Pb, Cu, Ag, Au | -- | -- | X | X | -- | -- | 107 | 51 |
| Pb, Zn, Ag, Au, Cu(Bi) |  |  | X |  |  |  | 265 | 38 |
| Pb, Cu, Zn, Ag | -- | -- | X | X | -- |  | 1,235 | 1,008 |
| Pb, Bi, Sb | -- | -- | -- | X | -- | -- | 126 | 126 |
| Pb, Zn | X | -- | -- | -- | -- | -- | 282 | 0 |
|  | 11 | 10 | 7 | 7 | 2 | 2 | 14,412 | 11,282 |

(a) Million gallons per year.

## TABLE 29. WATER USE DATA FOR LEAD AND ZINC MINES AND PLANTS

| Number | Total Intake, MGY | Discharge to Waste, MGY | Total Use(a), MGY | Indicated Recycle Ratio(b) | Mine and Concentrator Combination: Gallons Used per Ton of Metal | Gallons Consumed per Ton of Metal(c) | Distribution percent of intake(d): Process | Cooling | Boiler Feed | Air Pollution Control | Sanitary | Recirculation Ratios(f): Process | Cooling | Boiler Feed | Air Pollution Control |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Lead | | | | | | | | |
| Mine and Concentrator | | | | | | | | | | | | | | | |
| 1 | 330 | 330 | 330 | 1.0 | 11,200 | 0 | 66.6 | 22.2 | 0.6 | 5.6 | 5 | 1 | 1 | 1 | 1 |
| 2 | 238 | 238 | 306 | 1.3 | 12,000 | 0 | 63.3 | 28.3 | 0.3 | 5.0 | 3 | 1.5 | 1 | 1 | 1 |
| 3 | 357 | 318 | 472 | 1.3 | 10,660 | 864 | 89.2 | 3.0 | UK(f) | 7.4 | 0.5 | 1.2 | 2 | 2 | 2 |
| 4 | 474(g) | 473 | 473 | 1 | UK | UK | 88.6 | 11.1 | >0.1 | >0.1 | 0.2 | 1 | 1 | 1 | 1 |
| 5 | 350 | 348 | 69 | 1 | 11,481 | 286 | 87.5 | 2.5 | UK | UK | 10.0 | UK | UK | UK | UK |
| 6 | 99 | 0 | (h) | UK | UK | 41,520 | 95.2 | UK | UK | UK | 2.4 | UK | UK | UK | UK |
| 7 | 2,900 | 2,470 | 4,400 | 1.5 | 20,600 | 6,000 | 98.0 | 0.4 | 0.4 | 0.4 | 0.8 | 1.5 | 2 | 2.0 | 2.0 |
| Smelter | | | | | | | | | | | | | | | |
| 8 | 894 | 763 | 894 | 1 | 14,600 | 2,147 | 14.2 | 77.0 | >0.1 | 1.2 | -- | -- | -- | -- | -- |
| 9 | 264 | 37.8 | UK | UK | UK | 1,220 | 16.2 | 38.0 | 7.6 | 28.6 | -- | -- | -- | -- | -- |
| Smelter and Pyrometallurgical Refinery | | | | | | | | | | | | | | | |
| 10(i) | 107 | 50.8 | 801 | 9.5 | 9,210 | 647 | 10.4 | 83.3 | -- | -- | 6.3 | 7 | 1.8 | -- | 1.7 |
| 11(j) | 1,230 | 1,008 | 5,104 | 6.6 | 22,200 | 986 | 29.6 | 40.3 | -- | 29.1 | 1.1 | 4 | 8.8 | -- | 1.9 |
| Pyrometallurgical Refinery | | | | | | | | | | | | | | | |
| 12 | 126 | 126 | 189 | 1.5 | 1,310 | 0 | -- | 75 | -- | -- | 25 | -- | 1.7 | -- | -- |
| | | | | | | | Zinc | | | | | | | | |
| Mine and Concentrator | | | | | | | | | | | | | | | |
| 13 | 257 | 257 | 319 | 1.3 | 21,600 | 0 | 49.9 | 29.2 | -- | 4.2 | 16.7 | 1.6 | 1 | -- | 1 |
| 14 | 303 | 303 | 823 | 2.6 | 13,500 | 0 | 98.6 | -- | -- | -- | 1.4 | 2.5 | 1 | -- | 1 |
| 15 | 1,299(k) | 122 | 691 | 1.0 | 17,700 | UK | 76.0 | 15.9 | >0.1 | 6.3 | 1.7 | 1 | 1 | -- | 1 |
| Smelter | | | | | | | | | | | | | | | |
| 16 | 72.2(l) | 19.6(m) | 60.2 | 1.2 | 1,200 | 1,050 | 41.6 | 19.4 | 0.1 | -- | 38.9 | 1.5 | 1 | -- | 1 |
| Smelter, Refinery, and Acid Plant | | | | | | | | | | | | | | | |
| 17(n) | 693 | 341 | 18,900 | 27.3 | 156,000 | 2,907 | 25.1 | 50.1 | 20.0 | 1.7 | 3.1 | 20 | 4.4 | -- | 1 |
| 18(o) | 4,130 | 4,078 | 14,800 | 3.6 | 55,200 | 195 | 1.1 | 36.2 | 1.0 | 61.0 | 0.7 | 36 | 4.4 | -- | 2.6 |

(a) Intake plus recycle.
(b) Intake plus recycle ÷ intake.
(c) Intake-discharge ÷ tons metal produced.
(d) As reported or calculated from data.
(e) Total water used ÷ fraction of new water in total, 1 indicates no recycle.
(f) UK = Unknown.
(g) Mine water.
(h) Recirculation practiced but data not reported.
(i) No sulfuric acid plant included.
(j) Sulfuric acid plant included.
(k) Reported intake but does not coincide with reported use.
(l) Reported intake but only 50.4 MGY can be accounted for.
(m) Discharge to ground.
(n) Electrolytic refinery.
(o) Pyrometallurgical refinery.

effects on the external- or internal-water-use patterns. The variations in individual plant systems, design, and practice have greater effects on water usage than the presence or absence of an acid plant.

The lead and zinc smelter-refinery combinations reported relatively lower water requirements. In four out of the five zinc or lead refineries responding, and in the industry in general, smelting and refining are carried out in the same plant. Three out of the five operations for which data are listed include sulfuric acid plants. The water-use characteristics of the zinc refining operations (17 and 18) are distinguishable one from the other on the basis of climate and type of operation. The electrolytic zinc refinery (17) is in an arid climate and shows low intake, low discharge, very high use and consumption, and high recirculation rates. The other zinc refining operation (18), located in an area of plentiful rainfall, which refines zinc by distillation, shows much higher intakes and discharges but lower use and consumption.

Data on the lead smelter and refinery operations (10 and 11) show the effects of the difference of plant design and capacity on water usage. Both are situated in the same general area of the country and employ blast-furnace smelting and fire refining. The second plant listed (11) operates a sulfuric acid plant in conjunction with smelting and refining.

Data on a single lead-refining operation (12) indicated that water was used only for cooling and sanitary purposes. All water was obtained from and returned to a municipal supply and sewer system.

## Waste-Water Sources and Characteristics

The sources of waste water in the lead-zinc industry are listed in the following tabulation:

- Water Treatment
    - Clarification sludges
    - Sand filter backwash
    - Water-softening backwash or sludges
    - Ion-exchange regeneration wastes
- Sanitary Wastes
- Process Water (smelters and refineries)
    - Slag granulation waste water
    - Gas scrubbing waste water
    - Spent electrolyte
- Direct Cooling Water
    - Steam jet ejector condensate
- Cooling Waters
    - Indirect once through cooling water
    - Cooling tower blowdown
- Miscellaneous
    - Boiler blowdown.

The quantity of waste water discharged from lead and zinc plants has been discussed in the previous section. The compositions of waste waters and the receiving streams reported in the survey are shown in Table 30.

Although these data represent only a small segment of the lead-zinc operations, they provide an insight into the natures and types of wastes that are generated by the industry.

Effluents from the tailings ponds of mine-concentrator facilities apparently do not pose serious problems in general. There is a suggestion however that the effluents from some concentrators might contain concentrations of cadmium and lead at or near the level of concern.

Smelter and refinery effluents have a much greater pollution potential than those from concentrators with respect to both cadmium and lead.

Waste-treatment practice in the smelter-refinery segment of the industry ranged from virtually none, through simple settling, to neutralization-flocculation-settling.

Table 31 summarizes the treatment practices reported by the lead-zinc contributors to this study.

## Water Costs

Data obtained on water costs in the lead-zinc industry were sparse, nondefinitive, and certainly not representative of the industry. Water costs for the group of nonferrous industries covered in this section of the report are discussed in a later section.

## Current Plans

Lead-zinc producers in many cases echoed copper producers in reporting current plans for waste-treatment improvement and water management. Increased reuse of water by recycling, the substitution of polyelectrolytes for lime as a flocculant for tailings, the complete recycle through settling and cooling ponds for smelter wastes, segregation of contaminated process streams from clean water streams, neutralization of sulfuric acid plant wastes, recycling of wash water and electrolyte spills in lead and zinc refineries, an investigation into the feasibility of deep-well injection, all these are proposed and in some cases are being presently pursued.

TABLE 30. COMPOSITION OF WASTE WATERS AND RECEIVING STREAMS IN LEAD-ZINC METALLURGICAL PROCESSES (in mg/l)

| | Mine Concentrator Effluents(a) |
|---|---|
| pH | 5.0-8.0 |
| As | 0.0-0.09 |
| Cd | 0.0-0.02 |
| Cu | 0.004-0.3 |
| Fe | 0.04-1.5 |
| Mn | 0.0-0.8 |
| Pb | 0.0-0.18 |
| Zn | |

Lead Smelters, Refineries

| | I(b) | | | II(c) | | III(d) | | |
|---|---|---|---|---|---|---|---|---|
| | Upstream | Outfall | Downstream | Intake | Receiving Stream | Intake | Neutralized Acid Plant Water | Other Waste Water |
| pH | 7.6-8.1 | 7.4-8.2 | 7.6-8.2 | 7.8 | 7.8-11.1 | 7.2 | 5.0 | 8.6 |
| As | 0.11 | 0.15-0.46 | | | | -- | -- - | -- |
| Cd | 0.002 | 0.02-1.09 | 0.03-0.113 | | 0.0-0.007 | -- | 7.7 | 0.5 |
| Cu | 0.13 | 0.13 | 0.13 | 0.34 | 0.0-0.015 | -- | 0.06 | 4.0 |
| Fe | -- | -- | -- | 0.8 | 0.0-0.03 | 5.0 | 7.4 | 1.3 |
| Mn | -- | -- | -- | 0.2 | 0.004-0.05 | 0.9 | 0.7 | 0.5 |
| Ni | -- | -- | -- | -- | | -- | 0.2 | 0.06 |
| Pb | 0.03-0.03 | 0.07-0.157 | 0.03-0.05 | 0.14 | 0.0-0.01 | -- | 0.5 | 11.0 |
| Zn | 0.08-0.13 | 0.11-2.00 | 0.08-0.43 | 0.019 | 0.01-0.048 | -- | 8.0 | 2.0 |
| $SO_4$ | | | | 6.5 | 9.2-23.0 | 126 | 960 | 200 |

Zinc Smelters, Refineries

| | I(e) | II(f) | |
|---|---|---|---|
| | Effluent | Intake | Discharge |
| pH | 7.7 | 5.0-7.0 | 5.2-6.8 |
| As | -- | -- | -- |
| Cd | 0.39 | -- | 0.9 |
| Cu | -- | -- | 0.02-1.35 |
| Fe | 1.0 | 1.0-1.2 | 1.3-19.7 |
| Mn | -- | 0.4-1.0 | 0.4-1.75 |
| Pb | -- | -- | -- |
| Zn | 8.5 | 5.7 | 18-25 |
| $SO_4$ | | 136-179 | 182-291 |
| CN | | -- | 1.3-1.5 |
| Dissolved Solids | 583 | 372-391 | 304-534 |
| Suspended Solids | 10 | 14-18 | 14-164 |

Footnotes on following page.

Footnotes for Table 30.

(a) From tailings ponds.

(b) Company surveyed effect of waste discharge on stream; outfall was combined process and cooling water. Major contributant to process water impurities was effluent from "gas conditioning" operation in which fumes and dusts were "moisturized" by spraying with water before entering electrostatic precipitator. Spray water collected in sump below conditioner and discharged.

(c) Company studied contribution of waste to stream over and above background impurities by analyzing intake water and the receiving stream below the outfall. Major source of contamination in effluent was water discharged from slag granulation operations.

(d) Company operates lead smelter in conjunction with sulfuric acid plant. Provided data on intake water, neutralized acid plant water prior to discharge, and "other"waste water, which includes slag granulation and cooling water.

(e) Combined waste stream from zinc smelter includes coke plant, cooling water, gas scrubbers, spills, clean-up, etc. No acid plant.

(f) Zinc smelter in conjunction with sulfuric acid plant. Analyses show composition of water supply and combined waste discharge.

TABLE 31. WASTE WATER TREATMENT PRACTICES IN LEAD-ZINC SMELTING AND REFINING OPERATIONS

| Primary Product | Smelter | Refinery | Acid Plant | Power Plant | Industrial Waste Water Amounts, MGY | | Treatment Method | Type of Waste Water | Receiver |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Untreated | Treated | | | |
| Pb | X | -- | -- | -- | 395. | 368 | Settling | Mixed plant wastes | Surface |
| Pb | X | -- | -- | -- | 12.5 | 25 | Settling | Mixed plant wastes, cooling, etc. | To irrigation |
| | | | | | | 25 | Evaporation | Mixed process waters | -- |
| Zn | X | -- | -- | -- | -- | 190 | Settling | Mixed process, cooling, etc. | Surface |
| Zn | X | X | X | X | 2611. | 1414 | Coagulate and settle | Mixed acid plant, cooling, etc. | Surface |
| Zn | X | X | -- | -- | 0 | Discharge | Not given | -- | -- |
| Pb | X | X | -- | -- | 9-4 | 25.2 | Neutralization | Acid plant water | Surface |
| Pb | X | X | -- | -- | | 45.5 | Settling | Slag granulation | Surface |
| Pb | -- | X | -- | -- | 126 | -- | None | Mixed waste waters | Sewer |
| Zn | -- | X | -- | -- | 319 | -- | None | Mixed waste waters | Estuary |

# SECTION XV

## DISCUSSION

In the foregoing sections of this report an effort has been made to group appropriately the findings of the study on water usage; waste water sources, characteristics and quantities; waste treatment practices; and research needs.

In the belief that a general overview of the segments of the nonferrous industry dealt with in this section will provide an additional basis for insight into the general water and waste problems, this summarizing discussion section is included. It covers:

(1) Waste water treatment practices

(2) Water costs

(3) Current problems and future research needs

(4) Current plans of the industry.

### Waste Water Treatment Practices

The data obtained have shown that the approximately 50 plant operations discussed in this report currently discharge slightly over 56-1/2 billion gallons of water per year. The characteristics of these waste waters have been discussed in previous sections of this report. This section of the report will deal in a general fashion with how this waste water is treated.

Of the 50 operations involved, 14 (or 28 percent) reported zero discharge. These operations, all located in dry climates, employ tailings ponds to close the water circuit, with high evaporation rates and possibly ground seepage making discharge unnecessary. Included in these 14 facilities with zero discharge of water water were 12 mines and concentrators, 1 copper leaching operation, and 1 smelter. In terms of treatment methods, all 14 of these plants employed evaporation as a waste treatment method. The application of this method is limited by geographical/climate considerations.

Tailings ponds also were used by plants in areas of plentiful water for sedimentation of solids and in some cases as a reservoir for recirculation of water. These discharged about 38 billion gallons of water per year or 67 percent of the 56-1/2 billion gallons of total discharge. Thus, the tailings pond treatment practice appears to be the most predominant practice, serving not only to provide evaporation and clarification but also to permit recycling of water.

A compilation of the waste treatment practices used in these segments of the nonferrous industry is shown in Table 32. This listing shows the types of operations, treatment practices and amounts, the receivers of discharges and some indication of the characteristics of the waste waters treated by different methods. Table 33 shows the overall statistics on treatment practices. The data as gathered from the responses of industry show that 77.7 percent of all waters discharged are given some treatment by the metallurgical operations included in this study. Treatment in tailings ponds is, as stated before, the predominant method of treatment. Other forms of settling, in at least one case aided by coagulating agents, and dilution before release account for the next largest amounts of water.

TABLE 33. SUMMARY OF WASTE WATER TREATMENT PRACTICES

| Treatment Method | Amount Treated, MGY | Percent of Total |
|---|---|---|
| Tailings Pond | 37,984 | 69.2 |
| Other Settling | 2,043 | 3.7 |
| Dilution | 2,016 | 3.7 |
| Neutralization | 25 | 0.1 |
| No Treatment | 12,798 | 23.3 |
| Total Discharge | 54,866 | 100.0 |
| Evaporated | 248 | |

Sanitary wastes were common to all of these operations. Of 48 plants, intake of 2,116 MGY or about 2 percent of the total intake of 112,900 MGY was used for sanitary purposes. Of 36 cases in which this flow could be traced, 426 MGY per year of sanitary waste water returned to the following receivers:

| | |
|---|---|
| 5 plants - municipal sewers | 179.4 MGY |
| 6 plants - surface waters | 196.8 MGY |
| 3 plants - estuaries | 49.5 MGY |

All of the water discharged to surface waters and estuaries was treated in some manner before discharge.

The remainder of all intake "sanitary" water was traced to recirculation, evaporation, or ground seepage. The remaining plants used the following practices:

TABLE 32. SUMMARY OF REPORTED WASTE TREATMENT PRACTICE

| Primary Product | Leaching | Mine | Concentrator | Smelter | Refinery | Acid Plant | Power Plant | Waste Quantity, MGY Untreated | Waste Quantity, MGY Treated | Treatment Method | Type of Waste Water | Receiving Water |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Cu |  | X(a) | X(a) | X(a) |  |  |  |  | 0 | Evaporation;seepage | -- | Groundwater |
| Cu |  |  |  | X(b) |  |  |  |  | 0 | Ditto | -- | " |
| Cu | X(c) |  |  |  |  |  |  |  | 0 | " | -- | " |
| Cu-Pb-Zn |  | X(d) | X(d) |  |  |  |  |  | 38,000 | Settling, recirculation |  | Streams, estuaries, etc. |
| Cu |  |  |  | X |  |  | X | 467 |  | None, direct discharge | Cooling, process | Surface water |
| Cu |  |  |  | X |  |  |  |  | 216 | None(e) | Boiler, cooling tower blowdown, sewage | Ditto |
| Cu |  |  |  | X |  | X |  | 1134 |  | None | Cooling, acid plant water | " |
| Pb |  |  |  | X |  |  |  | 395 | 368 | Settling | Mixed wastes, cooling, process | " |
| Pb |  |  |  | X |  |  |  | 12.5 | 25 | " | Ditto | Irrigation |
| Zn |  |  |  | X |  |  |  |  | 190 | " | " | Surface |
| Zn |  |  |  | X | X | X | X | 2611 | 1414 | Coagulation, settling | " | Surface |
| Pb |  |  |  | X | X |  |  | 9.4 | 25.2 | Neutralization | Acid plant water | Surface |
| Pb |  |  |  | X | X |  |  |  | 45.5 | Settling | Slag granulation | Surface |
| Cu |  |  |  | X | X | X | X | 4550(f) | 2016 | Dispersion | Acid plant water | Estuary |
| Cu |  |  |  |  | X |  |  | 1718(g) |  | None | Cooling water | Estuary and sewers |
| Cu |  |  |  |  | X |  |  | 0 | 0 |  |  | Irrigation |
| Cu |  |  |  |  | X |  |  | 698(h) |  | None | Cooling water and blowdown | Sewer and Estuary |
| Cu |  |  |  |  | X |  |  | 730 |  | None | Mixed | Estuary |
| Cu |  |  |  | X |  |  |  | 50.8(i) |  | None | Process, cooling, boiler blowdown | Estuary |
| Cu(j) |  |  |  |  | X |  |  | 297 | 6.6 | None | Spent acid | Not reported |
| Pb |  |  |  |  | X |  |  | 126 |  | None | Mixed waste | Sewer |
| Zn |  |  |  |  | X |  |  | 319 |  | None | Ditto | Estuary |

(a) 14 operations in arid climates including various combinations of mines, concentrators, and smelters.
(b) 1 copper smelter in arid climate
(c) 1 copper leaching operation in arid climate.
(d) 12 mine-mill combinations.
(e) Plant evaporated additional 249 MGY.
(f) Cooling water.
(g) Includes 54 MGY to sewers.
(h) Includes 306 MGY of cooling water to sewers and 392 MGY of condensate and blowdown to estuary.
(i) Includes 28 MGY process water, 175 MGY cooling water, and 5.3 MGY boiler blowdown.
(j) Plant employs some evaporation for process wastes.

17 - plant operated septic tanks or lagoons
3 - treat and recirculate to leach operation
2 - treat and recirculate to tailings ponds

Only a few examples of cost data for plant operated sewage treatment were reported in segregated form and are listed below:

| Treatment Method | Amount Treated, MGY | Capital Investment, $1000 | Operating and Maintenance Costs |
|---|---|---|---|
| Package treatment plant | 5.2 | -- | $0.11/1000 gal |
| Package treatment plant | 21.6 | 54 | $0.19/1000 gal |
| Clarifiers, digesters, oxidation ponds | 73 | -- | -- |
| Aeration, settling, percolation, dilution | | | |
| Septic tank, chlorination, oil skimming | 13.5 | -- | $2.77/1000 gal |
| -- | 24.5 | -- | $0.82/1000 gal |
| Package treatment plant | 19.6 | 53 | $0.21/1000 gal |

Dilution, however, was reported by only one respondent.

It should be pointed out that there is some uncertainty about the cases shown in Table 32 in which treatment is reported as "none". Many of the nominally untreated wastes consisting of mixed plant waste waters may have received some treatment as by mixing or by settling and through misunderstanding; these were not considered treatments by the respondent.

## Water Costs

Data obtained were not adequate to relate water costs to a specific segment of the industry.

The cost data assembled by this review covered various categories: costs of supply, specific treatment costs for both intake and waste waters, and total water costs. The reported total water costs are listed in Table 34. Intakes are rounded to one significant figure to conceal specific plant identities as are the larger intakes. With only three exceptions, capital investment in total water systems for the plants increases with increasing intake, a not unexpected type of behavior. However, the reported operating and maintenance costs for the various water systems show little consistency with size of operation. The lowest water cost, $0.003/1000 gallons, was reported for the uses of salt water pumped from and returned to an estuary, and used only for cooling. The highest cost reported, $0.33/1000 gallons, was for a mining and concentrating operation in the southwestern desert region. The water costs of plants purchasing from municipal supply systems ranged from $0.08 to

$0.26 per 1000 gallons. One respondent defined total water costs as $0.03 per ton of ore processed by flotation concentration and $0.039 per 1000 gallons of total water pumped.

TABLE 34. REPORTED TOTAL WATER COSTS

| Intake, MGY[a] | Capital Investment, $ | Operating and Maintenance Costs, $/1000 gal |
|---|---|---|
| <5,000 | 27,883,000 | -- |
| <5,000 | 3,533,000 | 0.03 |
| 5,000 | 2,713,183 | 0.07 |
| 4,000 | -- | 0.04 |
| 4,000 | 950,000 | 0.01 |
| 2,000 | 600,000 | 0.05 |
| 2,000 | -- | 0.08[b] |
| 1,000 | 250,000 | 0.02 |
| 1,000 | 933,000 | 0.12 |
| 800 | -- | 0.33 |
| 700 | -- | 0.10 |
| 500 | -- | 0.27 |
| 500 | -- | 0.003[c] |
| 500 | 95,000 | 0.01 |
| 400 | -- | 0.08 |
| 400 | 150,000 | 0.13 |
| 300 | -- | 0.04[b] |
| 300 | 185,152 | -- |
| 200 | -- | 0.26[b] |
| 100 | -- | 0.09 |
| 100 | 230,000 | 0.21 |
| 70 | 43,568 | 0.06 |

(a) Rounded to one significant figure.
(b) Purchased municipal water, all other are independent systems.
(c) Obtained from estuary.

The reported costs of water treatment before use are listed in Table 35. Chlorination of potable water was commonly practiced at most plants with independent water supplies. Only two plants reported chlorination of all plant intakes. The two examples of costs for chlorination range from about one to three cents per 1000 gallons, the cost varying, in only two examples, inversely with amount treated.

The reported costs for softening and other treatment of boiler feed water varied from about 1-1/2 to 80 cents per 1000 gallons, with again large variations and no consistent pattern to the variations. Boiler feed water treatment practices included (1) the use of condensate from evaporators, (2) ion exchange demineralization, (3) chlorination, and (4) chemical softening, using such additions as polyphosphates, sulfites,

TABLE 35. WATER TREATMENT METHODS AND COSTS

| Amount Treated, MGY | Type or Use of Water | Treatment Method | Capital Investment (for specific treatment), $ | Operation and Maintenance Costs, $/1000 gallons |
|---|---|---|---|---|
| 4000 | Plant supply | Chlorination | -- | 0.008 |
| 20 | Potable | " | | 0.03 |
| 10 | Boiler feed | -- | -- | 0.72 |
| 40 | Ditto | Demineralization | 135,000 | 0.79 |
| 100 | " | Chemical softening | -- | 0.014 |
| 100 | " | -- | 7,100 | 0.28 |
| 100 | " | Sulfates and phosphates added | -- | 00.365 |

sodium chloride, dolomitic lime, and magnesium oxide. The treatment costs associated with boiler feed water were higher than any other treatment cost except sewage treatment, were applied to relatively small fractions of total intakes, and were more often recirculated.

The specific cost data reported for waste treatment processes is listed in Table 36. Treatment in tailings ponds is the cheapest of the three treatments shown, showing costs from one to five cents per 1000 gallons of discharge. The costs of other forms of settling, i.e., those used by operations other than flotation concentrators were reported by only two respondents. Reports varied widely.

TABLE 36. WASTE WATER TREATMENT METHODS AND COSTS

| Amount Treated, MGY | Treatment Method | Capital Investment, $ | Operation and Maintenance Costs, $/1000 gallons |
|---|---|---|---|
| 300 | Tailings pond | 1,270,000 | 0.017 |
| 500 | Ditto | 50,000 | 0.048 |
| 2500 | " | 208,377 | 0.020 |
| 7000 | " | < 10,000,000 | 0.007 |
| 1000 | Settling[a] | 363,000 | 0.097 |
| 1000 | " | 25,000 | 0.005 |
| 5 | Sewage Plant | 54,000 | 0.11 |
| 20 | Ditto | -- | 0.19 |
| 20 | " | 53,000 | 0.21 |
| 20 | " | -- | 0.82 |

(a) Coagulating agents added.

Treatment costs for sanitary wastes were reported in separate form in four cases, with the cost as shown previously, ranging from about 10 to 80 cents per 1000 gallons treated.

The major conclusion derivable from a consideration of the reported data is that a better and more reliable report of costs would require that all operations be costed on a uniform basis, with considerably more detailed review of internal costs and operations than was possible in this study. Some respondents merely noted that water costs were distributed among various operational costs and not broken down for distinct operation. It also appeared that most operators consider waste water treatment an integral part of plant operation, the preponderance of replies noting total water costs with no breakdown of the specific costs of waste water treatment.

Certainly, more important than cost or method is the effectiveness of the treatment. In only a few cases was effectiveness of treatment method rated, in terms other than "satisfactory". Bound up in the term "effectiveness" is the concept of external standards. Because of the current circumstances, what has been "satisfactory" in the past may not be now or in the near future.

Only two examples of quantitative measurement of effectiveness of treatment were submitted in this survey. The first example quoted here is from a large copper concentrating and smelting complex with high reported capital investments in waste treatment facilities and very low operating and maintenance costs:

| Operation | Substance | Treatment | Reduction, percent |
|---|---|---|---|
| Concentrator | Suspended solids | Settling, lime | 99.99 (+) |
| " | Dispersant | " " | 99.20 |
| " | Collector | Actual process | 99.99 (+) |
| " | Promoter | " " | 99.99 (+) |
| " | Frother | " " | 99.00 (+) |
| " | Flocculant | Precipitation, settling | 99.50 |
| Sewage treatment | Biological oxygen demand | Digestion, filtration | 78.00 |
| Ditto | Suspended solids | Settling, filtration | 85.00 |
| " | Pathogenic bacteria | Chlorination | 99.00 (+) |

The second example is from a zinc smelting operation reporting high investment and relatively high operating and maintenance costs:

> "Two parallel systems, each comprised of a number of settling lagoons, are employed for the removal of zinc-bearing materials and other suspended matter. Coagulant aids are used to promote settling efficiency. Chlorides and cadmium-bearing wastes are also routed through these systems to enhance waste water quality. Effectiveness of treatment is as follows:

| Substance | Percent Removal |
|---|---|
| Suspended solids | 98+ |
| Zinc | 98+ |
| Cadmium | Undefined |
| Chlorides | Undefined |

## Current Problems and Future Research Needs

The current and future research needs expressed by industry covered a broad spectrum, including:

(1) Firm bases for the establishment of discharge water standards with particular respect to hazard levels of trace metal concentrations

(2) The development of standardized and adequate analytical techniques

(3) The development of new process technology to reduce discharges by increasing recycling, and

(4) Improved waste treatment processes for both industrial and sanitary waste with emphasis on metal and acid removal.

The statements from industry are summarized below, grouped according to major topic.

## Limits and Standards

A more scientific basis for setting metal limits in discharges is needed. This would require more accurate information on the hazard levels of heavy metal ions than now seems available. The setting of limits for the discharge of metals to harbors is a special problem. Some respondents discharging to harbors stated they were not aware of any serious problem at present, but if told that the pollutants carried by water effluents were too high they would take steps to reduce the levels.

## Analytical Techniques and Programs

Sufficiently precise and accurate procedures for determining trace components of the waste are available. These should be adopted to verify the very low concentrations of metals, etc., in settling pond effluents and to determine background concentrations in natural water sources.

The supply of capable inorganic analysts and biologists continues to lag behind the load being imposed by regulatory agencies in setting standards and limits on specific contaminants. Undergraduate and graduate level training and research need to be encouraged and supported in this most critical area. One respondent indicated that an extensive analytical campaign was begun before start-up of a plant, to establish background levels of critical components in natural waters of the area. After start-up the impact of the plant's discharge on water quality will be assessed to determine compliance with the state laws pertaining to water pollution.

## Specific Problems in Industrial Wastes

Some respondents indicated a definite need for the development of low-cost procedures to remove small to trace quantities of metals, such as Zn, Pb, Cd, As, and Sb from effluents to ensure full compliance with state standards. Others anticipated a need for the improved treatment and disposal of waste acidic solutions and wash waters from tank house and by-product plants containing $H_2SO_4$, HCl, $H_2SO_3$, Cu, $SO_4^{=}$, As, Sb, and trace metals. Improved oil separation was also cited as a need by some.

Storm water runoff was cited by one respondent from the southwest desert area as a contributant of acid and suspended solids to receiving streams. Seepage from lagoons into groundwater was stated to be an ill-defined but possibly significant problem.

## Sanitary Wastes

One respondent indicated that the existing concept of conventional, biological treatment of human wastes needs to be reexamined for the possibility of reducing costs involved in collection, treatment, pumping, etc. Another indicated it would be desirable to have available some method by which the sewage treatment effluent could be recycled as cooling water for metal-casting operations.

One general response dealt with the need for incentives to encourage research by industries to improve technology which would minimize the quantity and improve the quality of discharges. These incentives would be supplemental to those now in existence for waste treatment systems.

About 60 percent of the returns from industry indicated no research needs, either by omission of any reply or by an explicit statement to that effect. (About half of these, it may be remembered, have zero discharge). Probably reflecting the basis for the belief that no research was needed is the statement by one respondent operating a concentrator.

> "The main treatment will always consist of settlement of suspended solids, which is completely effective now. A large disposal area with a settling lagoon will always be needed, so no research or less costly method is indicated."

A summary of the positive responses discussed above is listed in Table 37.

TABLE 37. SUMMARY OF PLANTS AND RECOMMENDED AREAS OF FUTURE DEVELOPMENT WORK

| Type of Operation | Discharge, MGY | Topics Recommended for Future Work | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | Acid Wastes | Heavy Metal Removal | Oil Removal | Sanitary Wastes | Heavy Metal Hazard Limits | Analysis | Metallurgical Process Development |
| Mine-Concentrator | 1,446 | -- | -- | -- | -- | X | -- | -- |
| Ditto | | -- | -- | -- | -- | X | -- | -- |
| " | | -- | -- | -- | -- | X | -- | -- |
| " | | -- | -- | -- | -- | -- | X | -- |
| " | | -- | -- | -- | -- | -- | X | -- |
| Copper Mine, Mill, Smelter | 16,324 | -- | -- | -- | X | -- | X | X |
| Zinc Smelter | | X | X | -- | -- | X | -- | -- |
| Copper Refinery | | -- | X | -- | -- | -- | -- | -- |
| Ditto | | -- | X | -- | -- | -- | -- | -- |
| " | | X | X | X | X | -- | -- | -- |
| " | | -- | -- | -- | X | -- | -- | -- |
| Copper Mine-Concentrator | | -- | -- | -- | X | -- | -- | -- |

## Current Plans

Fourteen (or 28 percent) of the responding operations gave information regarding planning and/or the work currently under way to reduce the volume of waste water or to reduce pollutant levels. The comments from industrial operations are summarized in Table 38.

As shown in the table, only one copper leaching operation (5) and possibly one smelting operation (9) have plans which offer any possibility of increased product recovery. All other plans are directed at waste water control. No definitive costs were indicated in the responses. Nine of the fourteen plans include increased recycling and associated decrease of discharges. Four plans include possible total recycle, i.e., a closed water circuit with decreased intake and zero discharge. On the other hand, three tailings-ponds operators state the intent or necessity of continuing discharges and employing additional treatment methods. Two of the smelter-refinery type operations indicate plans for extensive waste treatment or disposal (deep well injection) facilities. Other cases indicate various combinations of process change, waste water reduction and recycling, waste water segregation, and additional treatment of some specific portions of waste water. The smelter-refinery type operations show concern for improvements in both sanitary and industrial waste water discharges.

The general trend in these plans is for increased recycle and decreased discharge. Although most of the plants reporting are in areas of plentiful rainfall, it is not unlikely that some, by the implementation of these plans, may achieve extremely low or possibly zero discharge of effluents, a situation that is now only attained by plants in desert climates, through evaporation and permeation.

If the trend, as expressed by these responses, is a general one in the industry, as it well may be, decided reduction in water usage and pollution can be expected.

As part of this program, the information obtained has been reviewed and assessed in terms of unit processes and associated waste waters. The numerous unit processes covered are presented in Table 39.

The approach has been to review each metal in terms of all unit processes, indicate whether water is used and follow with waste water characteristics and control status, wherever such information was obtained in the program. Also included in Table 39 are recommendations for the next action appropriate for each process step indicated.

The data indicate that there are many specialized problems but a brief discussion may aid in the understanding of the table entries. The recommendations are in terms of double objectives: (1) identifying needs for research, development, or demonstration to lend impetus to water quality improvement, and (2) assessing the approach of the study

TABLE 38. MEASURES UNDER STUDY OR IN EFFECT

| Respondent | Type of Operation | Waste Volume Reduction | Waste Treatment Improvements |
|---|---|---|---|
| 1 | Mine-Concentrator | Recirculation of all or part of tailing water | pH control |
| 2 | Mine-Concentrator-Smelter | No in-plant process change contemplated | a) Reduction of phosphate in sewage treatment plant effluent, by substituting other dispersants for polyphosphate now being used and by using effluent as source of plant nutrient in restoration of abandoned tailing area.<br>b) Investigation of polyelectrolytes as means for obtaining better settling of tailings. |
| 3 | Mine-Concentrator | Install flood-control dam above present pond-dam to minimize storm run-over and facilitate circulation | -- |
| 4 | Mine-Concentrator | Complete reuse of tailings water planned | Increased settling area |
| 5 | Copper leaching | Process changes to minimize loss of leach solution and enhance recovery | -- |
| 6 | Copper leaching | | Lime neutralization of stripped leach solution with recirculation of as much water as possible to the leach. |
| 7 | Smelter | Complete recirculation through settling pond with automatic pH control. Cooling sprays, etc. | |
| 8 | Smelter | Complete recirculation of cooling water now being discharged to sewers | Rerouting of sewer lines to separate clean water from wastes containing solids. Installation of settling facilities to remove these solids. |
| 9 | Smelter | Engineering studies to devise total recycle system | Solid-liquids separation facilities to permit recycle and by-product recovery |

Continued on following page.

TABLE 38. MEASURES UNDER STUDY OR IN EFFECT (continued)

| Respondent | Type of Operation | Waste Volume Reduction | Waste Treatment Improvements |
|---|---|---|---|
| 10 | Smelter | In present practice 350,000 gallons per day of once through cooling water are used for the external cooling of converter hoods. To be replaced by system incorporating recirculation of this water. | |
| 11 | Smelter-Acid Plant | | Neutralization of scrubber water from gas cleaners in acid plant |
| 12 | Refinery | Recycling of cathode wash water (32,000 gpd) and spills of electrolyte | Deep well injection of some wastes. Improved settling, filtration, etc. |
| 13 | Smelter | Engineering studies to increase rate of recycling | Engineering studies to improve domestic sewage treatment; expansion of settling ponds. Installation of monitoring systems. |
| 14 | Concentrator-Leaching | -- | Plant to be constructed in 1973 to neutralize, precipitate heavy metals, and clarify concentrator and spent acid wastes; adequately treat sanitary wastes. Expect to comply fully with state standards |

TABLE 39. ASSESSMENT OF INFORMATION OBTAINED IN TERMS OF UNIT PROCESSES AND FUTURE NEEDS

| Metal | Nominal or Overall Operation | Unit Operation or Process | Category or Use of Water | Waste Water Characteristics | Assessment of Reported Status of Waste Water Treatment or Water Pollution Control | Recommended Future Action |
|---|---|---|---|---|---|---|
| Copper | Mining | Open pit | Dust control | No waste water | No problem | None |
| | Mining | Underground | Mine drainage | Suspended solids, dissolved salts; sometimes sulfates and low pH. | Generally not a problem in the copper industry due to geographical and climatic conditions. | Waste load variable due to geological conditions; treatment has been achieved in Missouri Lead Belt by settling and holding; suggest demonstration on critical case. |
| | Concentrator | Ore crushing | Dust control | None | Retained in ore | |
| | Concentrator | Flotation | Process and transport medium | Suspended solids; flotation reagents; traces (< 1 ppm, of metal sulfides, cyanides, arsenic; 2000-4000 ppm total dissolved solids. High (alkaline) pH. | Sent to tailings pond; no problem in arid climates; in wetter areas metals contents may exceed local discharge standards; need technology transfer from desert areas to accomplish closed loop water system. | Suggest research to determine operative mechanisms in best and worst case; need educational effort related to spread of optimum tailings pond design and best practice (holding time, oxidation mechanisms; flocculents); need transfer of knowledge on recycle practice. |
| | | | | Modification of flotation | Modification of flotation reagent concentrations and compositions have been demonstrated or are being studied. | WQO program on reagent modification should be continued or accelerated. |
| | Mine-concentrator operations | Sanitary wastes | Domestic supply | Sanitary wastes | Usually sent to ground (i.e., seepage or evaporation); occasionally recycled through tailings pond, thus potential for recycle is demonstrated. | Need R&D on processes to treat sanitary wastes and recycle, both in the context of plant operation. |
| | | Power plants | Boiler blowdown, cooling tower blowdown | High chlorides, suspended solids, chromates | Usually recycled through tailings pond | Current data should allow setting of waste loads, treatment economics, and effluent standards; may need development of economical treatment to allow recycle. |
| | Leaching | Leaching | Spent liquor | Ferrous sulfates; low (acid) pH | Usually associated with desert operation; evaporated in holding ponds; occasional accidental spills; may be recycled through tailings pond or neutralized by the tailings pond before release. | Possible need for system to treat spills |
| | Smelting | Roasting | Calcine cooling | None | Evaporated | None |

TABLE 39. (continued)

| Metal | Nominal or Overall Operation | Unit Operation or Process | Category or Use of Water | Waste Water Characteristics | Assessment of Reported Status of Waste Water Treatment or Water Pollution Control | Recommended Future Action |
|---|---|---|---|---|---|---|
| Copper | Smelting | Reverberatory smelting furnace | Indirect cooling | Cooling water blowdown; high chlorides, suspended solids; chromates | A common waste water problem requiring the development of economical treatment methods to allow recycle; application demands high quality water. | See above |
|  | Smelting | Cast metal and mold cooling | Direct cooling | Suspended solids (carbonaceous or oily mold dressing; metal oxides) | Often times wasted; recycle or reuse demands treatment by settling and oil removal. | Need analyses to determine waste loads; treatment economics may be obtained from operating examples; effluent standards could then be set. |
|  | Smelting | Slag granulation | Process water | Suspended solids (silicates; inert oxides; possibly soluble trace element compounds, e.g., arsenates, antimonates). | Usually settled and recycled to same use. | Need analyses to determine waste loads |
| Copper | Electrolytic refining | Electrolytic refining | Electrolyte solution | Acid sulfate solution | Sometimes discharge with or without neutralization or dilution; strong need for cheap neutralization, alternate disposal or treatment allowing recycle. | Need some additional analyses to determine waste loads; neutralization is already practiced; costs and effluent standards could be developed fairly readily. |
|  |  | Power supply (DC rectifiers) | Indirect cooling | Same as above; chlorides, chromates, suspended solids | Need for treatment for recycle | See above |
|  |  | Furnaces<br>Copper melting<br>By-Product refining | Indirect cooling | Same | Same | Same |
|  |  | Metal casting | Direct cooling | Same as above (suspended solids, oils) | Same as above; needs more widespread application of settling and oil removal. | See prior case |
|  | By-Product metals (Se, Te, Ag, Au) | Gas scrubbing | Process | Dissolved trace element salts: arsenic, selenates, tellurium | Present fate largely unknown. | Need more information on industrial processing and for problem definition. |
|  |  | Electrolytic refining | Process | Dissolved salts | Usually recycled or carefully treated because of precious metal content. | Same |

TABLE 39. (continued)

| Metal | Nominal or Overall Operation | Unit Operation or Process | Category or Use of Water | Waste Water Characteristics | Assessment of Reported Status of Waste Water Treatment or Water Pollution Control | Recommended Future Action |
|---|---|---|---|---|---|---|
| Lead | Mining | Mining | Mine drainage | Dissolved salts of copper, lead, and zinc at ppm level | Generally discharged through tailings pond; metal contents are marginally near some effluent standards; enforcement of the most stringent standards would require economical treatment of very large volumes of water for low level impurities; tailings pond oxidation mechanisms recommended for study, as are carbonate precipitation mechanisms. Associated climate usually results in plentiful water supply. | See above |
| Lead | Flotation concentration | Flotation | Process water | Metals, flotation reagents, high pH, suspended solids | Trace metal removal same as above; polyelectrolytes aid settling but are added expense; cyanides readily oxidizable given sufficient holding time; long alcohols must be controlled to avoid eutrophication of some receiving waters; tailings pond mechanisms and design can be used effectively if designer is knowledgeable. | See above |
| Lead | Smelting | Sintering<br>Blast furnace<br>Drossing<br>Softening<br>Slag fuming | Indirect cooling | Same as above (chlorides, chromates, suspended solids). | Need for recycle treatment | See above |
| Lead | Electrolytic refining | Electrolytic refining | Spent electrolyte | Acidic | Practice unknown (1 or 2 plants operating in U.S.) | Need basic information on industrial practice and for problem definition. |
| | | Spills, equipment washdown | Process | Acid, high dissolved solids | Could be better controlled by plant drainage, redesign and segregation; some can be recycled. | Once controlled by drainage, segregation, this is generally a neutralization exercise; suggest setting a nil discharge standard for new plants and requiring update of old plants in some reasonable time. |

TABLE 39. (continued)

| Metal | Nominal or Overall Operation | Unit Operation or Process | Category or Use of Water | Waste Water Characteristics | Assessment of Reported Status of Waste Water Treatment or Water Pollution Control | Recommended Future Action |
|---|---|---|---|---|---|---|
| Zinc | Mining | Mining | Mine drainage | Same as above; trace metal contents and a higher incidence of trace impurities such as arsenic and cadmium. | As above; trace metal levels (ppm) possibly above some local standards. | See above |
| Zinc | Concentration | Flotation | Process | As above: suspended solids, trace metals, As, Cd, residual flotation reagents, and high pH. | As above; improved tailings pond management needed; or alternative economical treatment of large quantities of water to remove ppm level impurities. | As above |
| Zinc | Smelting | Roasting<br>Sintering<br>Retorting<br>Refining<br>Distillation<br>Liquation | Indirect cooling | As previously; chlorides, chromates, suspended solids. | Need wider application and/or improved treatment to allow recycle. | As above |
| Zinc | Smelting | Ingot casting | Direct cooling | As previously: suspended solids, oils. | Treatment needed for recycle | As above |
| Zinc | Smelting | By-Product cadmium recovery | Process; acid leach liquors | Acid, trace metal and impurity contents (As, Cd, In, Tl, Pb, Zu, Cu, metal sulfides in suspension). | Need for neutralization process to drop all trace impurities. | One plant has reported waste loads on unit process basis during this program; need additional process detail and effluent analyses; need R&D on neutralization or other treatment for complex-impurity streams. |
| Zinc | Electrolytic zinc | Leaching and electrolysis | Process; spent leach liquors, electrolytes; barren filtrates. | Generally acid, low pH, high sulfate | Information lacking (1 or 2 plants operating in U.S.). | Need basic information on current industrial practice and for problem definition. |
| Zinc | Electrolytic zinc | Spills, equipment wash water | Process | Acid; high sulfates and metals | Could be better controlled by plant drainage redesign and segregation; some can be recycled. | See above |
| Copper, lead, zinc | Smelting | Sulfuric acid plant | Indirect cooling | As previously | As previously | As above |
| Ditto | Smelting | Sulfuric acid plant | Gas cleaning (spray towers, cottrell sump, scrubber liquor, etc.) | Acid; high levels of arsenic, cadmium, copper, lead, zinc, selenium, tellurium, etc. | Practice variable; this stream is so conglomerate as to be only waste; this stream is variously disposed of by mixing, dilution, neutralization, or other means. A constant, recurring, and increasing problem as $SO_x$ control is advanced. More detailed examination of effectiveness of common neutralization processes is needed relative to many "impurity" type elements. | These waste liquors need R&D for complete impurity removal process; some analyses available; waste loads reported have wide range. |

to the point where unit process waste loads and effluent standards could be set. There follow some generalizations which may be drawn from the table.

The common wastes--sanitary and indirect cooling waters--have reached the situation where past published literature and current data could be used to set waste loads, treatment costs, and effluent standards. Indirect cooling water and boiler blow-down currently are being treated in some plants for recycle to the same circuits. These wastes are not unique to the metals industry. However, R&D is recommended for the development of a process for treating sanitary wastes for reuse in the context of an industrial plant which may have resources (waste heat or chemicals) or water quality demands different from those of municipal treatment plants. Such a process would decrease industrial water demands and discharges.

One of the general characteristics of smelting operations are acid plant waters, i.e., liquors from preliminary gas cleaning steps prior to manufacture of sulfuric acid. The nature of the waste water (reflecting individual ore compositions) would indicate complex, high, and variable waste loads, and the need for treatment processes capable of removing the complex wastes. Also identified in Table 39 are similar complex waste loads from by-product (Cd, In, As, Tl) metals recovery operations using chemical or hydrometallurgical processes. These waste loads are characteristic of by-product operations in the lead and zinc industry and of custom smelters handling fume and flue dust from other industries. The acid plant liquors (which will probably become more common as $SO_x$ control increases) and the by-product metal operation wastes appear to be compatible for simultaneous R&D studies of water treatment processes aimed at achieving satisfactory removal of all the by-product metal impurities from the complex waste.

Spent electrolytes appear as wastes in the copper, lead, zinc, gold, and silver industries. More analyses are required to establish waste loads or effluent standards. The possibility of recycle should be determined more clearly by a survey of industry, especially in the case of gold and silver parting plants, where no information was obtained.

Although equipment wash water and electrolyte spills were identified in this study as contributing to waste water, it is judged that the most effective means of control of these would be plant design and waste segregation.

Two other major types of waste water identified were mine drainage and flotation concentration effluent. Both these streams are high in volume and low in impurity content. The mixed response to this survey varied from immediate discharge--to treat and discharge (with varying treatment)--to total recycle, and would indicate that practice is not uniform throughout the industry. Thus, case studies are recommended of selected best and worst situations, with the evaluation of the importance of factors contributing to the most efficient performance of the better settling pond type operations (e.g., retention time, flocculants, oxidation promoting factors, or other factors).

At the time of this survey--which gathered data produced mostly in 1970--data allowing the calculation of unit waste loads existed for only a few of the unit processes identified, but industry was progressing in the accumulation of analytical data. A subsequent study should yield an increased amount of specific data.

## SECTION XVI

## ACKNOWLEDGMENT

The sections of this report dealing with waste-water sources, characteristics, amounts, and treatment practices are based largely on the contributions of data and information of producers of nonferrous metals. These contributions were made on a purely voluntary basis and at no cost to the project. The constraint of confidentiality does not allow the recognition of the contributors to this study on an individual or corporate basis, thus due acknowledgment must be given to the nonferrous metals industry in general.

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# SECTION XVII

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